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A TEXT-BOOK OF MEDICAL CHEMISTRY AND TOXICOLOGY

BY

JAMES W. HOLLAND, A.M., M.D., Sc.D.
EMERITUS PROFESSOR OF MEDICAL CHEMISTRY AND TOXICOLOGY, AND DEAN,
JEFFERSON MEDICAL COLLEGE, PHILADELPHIA

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IN

FILIAL RESPECT AND AFFECTION

PREFACE TO THE FOURTH EDITION

Since this book was written there have been many advances in medical chemistry. When deemed worthy of a place in a compendious work they have been incorporated with the text of the successive editions. No pretense of completeness can stand so long as the available space is limited to the dimensions of a handy volume. As in previous editions, so in this, attention is concentrated upon the essentials relating to medicine. Students whose minds may become quickened with desire for wider knowledge will know how to supplement its deficiencies by reference to more detailed treatises. While it has been the aim in this revision to maintain the plan and size that have so far met with favor, some enlargement is necessary to give a more satisfactory presentation of the aid now offered to diagnosis by the chemical laboratory. Extensions have been made to the sections on radium, thorium, uranium, and vanadium; on newer organic compounds of arsenic; the constitution of the carbohydrates and glucosids; the synthetic local anesthetics allied to cocain; the protective enzyms; the hormones, and an entire chapter on the feces. For more exact studies in metabolism and clinical chemistry the following additional tests have been described: Seleivanoff's for levulose, phenolsulphonephthalein for functional activity of the kidneys, Wassermann's for syphilis, Krokiewicz's for bile-pigment, Saloman-Saxl's for cancer, Volhard-Harvey's for chlorids, Folin's for urea, Folin and Macallum's for uric acid, Benedict's for sugar, safranin for sugar, Frommer's for acetone, Hart's for beta-oxybutyric acid, Folin's for ammonia, Tsuchiya's for albumen, Spiegler's for albumen, Meyer's for hemoglobin, Russo's for typhoid fever, Rimini's for formaldehyd, Abderhalden's for pregnancy. More than this word of acknowledgment is due to Professor Philip B. Hawk and Messrs. Melvin A. Saylor and Olaf Bergeim for helpful suggestions in this revision.

James W. Holland.

Philadelphia, Pa.,
October, 1914

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INTRODUCTION

METROLOGY

Chemistry deals with the properties and composition of substances and the operations which produce change of constitution.

Substances are known by their properties, such as color, form, hardness, weight, taste, odor, solubility, melting-point, boiling-point, and behavior in the presence of active chemicals. In studying the composition of a body, the properties of its components, and the operation of chemical force, there is frequent occasion to make estimates of volume and weight, and that relation between the two called *specific gravity*. *Metrology* is the science which deals with the means employed for this purpose.

Weights and the Balance.—In determining the quantity of matter present resort is had to the balance. In this instrument an inflexible horizontal beam is poised at its middle by a knife-edge, resting on a hard plate at the top of an upright support. The beam carries at each end a scale-pan suspended by cords or rods to the sharp-edged hook which freely swings from a steel pin.

In one scale-pan is put the body to be weighed, in the other, masses of matter called *weights*, which have been previously marked according to some standard. If the gravitation to the earth of the body to be weighed and the weight be equal, the vertical index oscillates evenly over its graduated arc, and the beam comes to an equipoise in a horizontal position.

The attraction of gravitation is directly proportionate to the mass. As the weight of a body is the effect of this downward force, it is plain that mass and weight will increase and diminish together. A double amount of matter requires a double weight to balance it, and one-half the weight equals one-half the mass or quantity of matter.

The Chemist's Balance.—In the ordinary balance the poise is not disturbed by slight variations in weight. Hence for commercial purposes, where time is to be saved and minute quantities are more or less unimportant, a less sensitive instrument is preferred. But in chemical analysis accuracy is to be desired above all things. For this purpose the beam of the balance is made as light as possible, the bearings are sharp and hard, the adjustments capable of being brought to the last degree of refinement, the instrument provided with appliances for arresting its action at will, and the whole enclosed in a glass case for protection from dust, for exclusion of moisture, and for the prevention of perturbations due to currents of air. The beam is usually divided by notches into tenths, so as to carry weights shaped as *riders*, which latter lessen in value as they are moved toward the center. For instance, a rider weighing 1 gram in the pan weighs .9 gram at the first notch from the pan, .8 gram at the second, .7 gram at the third, and .1 gram at the last. By this means a delicate chemical balance will indicate with distinctness $\frac{1}{20}$ of a milligram, and even less weights will influence it sufficiently to show a variation in the position of the index as it moves over the graduated arc.

Volume.—The quantity of space which a body fills is called its *volume* or bulk. In estimating volume, vessels of different shapes and sizes are used. These vessels, known as *measures* of capacity, are standardized by comparison with some unit.

Weights and Measures.—There are two systems of weights and measures in use among physicians and pharmacists. In the United States the prescriptions usually call for Apothecaries' Weights and Wine Measure with the common standard of the *grain*. Very rarely the decimal system, based upon the meter, is employed.

In the U. S. Pharmacopœia working formulas are given in the metric system. The regulations of the U. S. army require surgeons to write prescriptions in the decimal system. In time, as pharmacists grow accustomed to the easy calculations of a decimal system, it will probably win favor enough to supplant others now in vogue.

The U. S. Pharmacopœia Apothecaries' system of weights is derived from the *Troy* pound of twelve ounces.

Table of Apothecaries' Weight

20 grains	=	gr. xx	=	one scruple (℈j).
60 grains	=	℈iij (3 scruples)	=	one dram (ʒj).
480 grains	=	ʒviij (8 drams)	=	one ounce (℥j).
5760 grains	=	℥xij (12 ounces)	=	one pound (℔j).

In the British Pharmacopœia and in commercial transactions of druggists in this country the weights used are the *Avoirdupois* pound, ounce, and grain.

If the difference in the value of the terms ounce and pound, as used in the United States and in Great Britain, be not recognized, serious errors may be committed. As important medical works are printed in both countries, addressed in the same language to readers in both, it is to be regretted that there should exist this difference in terminology where uniformity and precision are especially to be desired. The special amount of the Avoirdupois ounce is usually indicated by a sign different from that employed in the Apothecaries' system: Thus *one oz.* stands for 437.5 grains; while ℥j means 480 grains.

Table of British Pharmacopœia Avoirdupois Weight

437.5 grains	=	one ounce (1 oz.).		
7000 grains	=	16 oz.	=	one pound com. (1 lb.).

The *Measures of Capacity* employed in the U. S. Pharmacopœia are derived either from the wine gallon or from the metric system.

Table of Wine Measure (U. S. P.)

1 minim	=	♏j			=	0.95 grains of water.	
60 minims	=	♏lx	=	fʒj (fluidram)	=	57.0 "	"
480 minims	=	fʒviij	=	f℥j (fluidounce)	=	456.4 "	"
7680 minims	=	f℥xvj	=	Oj (octarius or pint)	=	7273.6 "	"
61440 minims	=	Oviij	=	cong. (congius or gallon)	=	58328.0 "	"

Originally it was intended that one minim of the standard fluid, water, should weigh one grain. In fact, as stated in the table, under ordinary conditions it weighs 0.95 grains, while the fluidounce weighs only 455.7 grains. There is a much wider discrepancy between the pint of 16 fluidounces and the pound of 12 Troy ounces. In order to make terms of weight and measure more easily convertible the British Pharmacopœia uses a system in which the fluidounce of water weighs an Avoirdupois ounce of 437.5 grains. This system is given below:

Table of Imperial Measure (B. P.)

1 minim	= min. j		=	0.91	grains of water.
60 minims	= fl. dr. j	= ♏︎lx	=	54.68	" "
480 minims	= fl. oz. j	= f℥viij	=	437.50	" "
9600 minims	= Oj	= f℥xx	=	8750.00	" "
76800 minims	= cong. j	= Oviij	=	70000.00	" "

A pint of water is not a pound in the Apothecaries' system, for the Troy pound has 12 ounces, while a Wine Measure pint has 16 ounces. But the Avoirdupois or commercial pound is 16 ounces, which is nearer the weight of a pint of water, though not exactly equivalent. The pint of water weighs 7291.2 grains, though the pound weight itself is equal to only 7000 standard grains.

Approximate Measures

A wineglassful	is equivalent	to about	2 fluidounces.
A tablespoonful	"	"	½ fluidounce.
A dessertspoonful	"	"	2 fluidrams.
A teaspoonful	"	"	1 fluidram.

The **metric system** has the great advantages of a common unit for measures of weight, capacity, length, and surface, thus permitting easy conversion of one into terms of another.

Not only is measuring more easily done than weighing; it is also, as a rule, more accurately done. The facility in calculation afforded by the metric system is especially seen in the conversions of volumetric analysis which enable the analyst, by careful measurement, to dispense with the weighing of precipitates. All the benefits that accrue to arithmetic computations by a decimal system of counting (now universal) is shared by our American division of coins, and will be further extended wherever the metric system of weights and measures is adopted. The natural conservatism of the English race has delayed its general adoption in commerce, in medicine, and in pharmacy, but in chemical and physical calculations it is now almost universally employed.

Metric Units.—The unit of length, called a *meter*, is the length of a standard bar of metal which was supposed to be equal to one ten-millionth part of the distance from the equator to the pole. The meter is really the length of a certain bar of platinum kept by the Department of Weights and Measures in Paris.

The unit of capacity, called a *liter*, is the cube of a tenth part of a meter.

The unit of weight, called a *gram*, is the weight of so much distilled water at its maximum density (4° C.) as will fill a cube of the one-hundredth part of a meter. In taking this cubic centimeter of water as a unit of weight a simple and very desirable relationship is established between weights and measures.

The unit of surface, called the *are*, is the square of ten meters.

Decimal Table

In giving names to the decimal multiples a Greek numeral is prefixed; while those of the subdivisions are formed from Latin words signifying the decimal fractions.

	Length.	Weight.	Capacity.
1000 =	kilometer	kilogram	kiloliter.
100 =	hectometer	hectogram	hectoliter.
10 =	decameter	decagram	decaliter.
1 =	*Meter*	*Gram*	*Liter.*
.1 =	decimeter	decigram	deciliter.
.01 =	centimeter	centigram	centiliter.
.001 =	millimeter	milligram	milliliter.

As a rule, the terms used are the kilometer, kilogram, kiloliter, the meter, gram, liter, and the millimeter, milligram, cubic centimeter, or milliliter.

Measures of Length

1 meter = 10 decimeters = 100 centimeters = 1000 millimeters.
1 meter = 1.09363 yards = 3.2809 feet = 39.3709 inches.

Measures of Capacity

1 cubic meter = 1000 liters = 1,000,000 cubic centimeters = 1,000,000,000 cubic millimeters.
1 liter = 61.02705 cubic inches = .035317 cubic foot = 2.1134 pints = .22097 gallon.

Measures of Weight

1 gram = weight of 1 c.c. of water at 4° C.
1 kilogram = 1000 grams = 100,000 centigrams = 1,000,000 milligrams.
1 kilogram = 2.20462 pounds = 35.2739 ounces = 15432.35 grains.

Solids.		Exact equivalent.
$\frac{1}{10}$ grain	=	0.006479 gram.
$\frac{1}{8}$ "	=	0.008098 "
$\frac{1}{6}$ "	=	0.010798 "
$\frac{1}{4}$ "	=	0.016200 "
$\frac{1}{3}$ "	=	0.021599 "
$\frac{1}{2}$ "	=	0.032399 "
1 "	=	0.064798 "
5 grains	=	0.3230 "
10 "	=	0.6460 "
1 scruple (20 grs.)	=	1.2960 "
1 dram Troy (60 grs.)	=	3.888 "
1 ounce Troy (480 grs.)	=	31.103 "
1 ounce Avoirdupois (437.5 grs.)	=	28.350 "

Measures of Weight

Liquids.		Exact equivalent.
1 minim	=	0.061 cubic centimeter.
1 fluidram	=	3.697 cubic centimeters.
1 fluidounce	=	29.574 " "
4 fluidounces ($\frac{1}{8}$ liter)	=	118.295 " "
8 " ($\frac{1}{4}$ ")	=	236.590 " "
1 pint ($\frac{1}{2}$ liter)	=	473.180 " "
1 quart	=	.946 liter.

To facilitate mental translations from the decimal system to the one used in this country, and for rapid reference, the following approximate equivalents are recommended as easy to memorize:

APPROXIMATE EQUIVALENTS

1 meter	=	3 feet, $3\frac{3}{8}$ inches.
1 kilometer	=	$\frac{3}{5}$ mile.
1 millimeter	=	$\frac{1}{25}$ inch.
1 liter	=	2.113 pints (U. S.), or about 1 quart.
1 kilogram	=	$2\frac{1}{5}$ pounds, Avoirdupois.
1 gram	=	$15\frac{1}{2}$ grains, or about $\frac{1}{30}$ ounce.
1 milligram	=	$\frac{1}{65}$ grain.
1 are	=	a square, the side of which is 11 yards.

On the basis of calculating 65 milligrams to make a grain and 32 grams to the ounce, Troy, the following round numbers may be of service in prescription writing, being sufficiently accurate for that purpose:

♏j or grain j	=		06 gram or cubic centimeter.
f℥j or ʒj	=	4	grams or cubic centimeters.
f℥j or ℥j	=	32	" " "

The line is used instead of a decimal point, the figures standing for solid grams or fluid cubic centimeters. A teaspoon holds about 5 c.c. and a tablespoon about 20 c.c.

Specific Gravity.—If we take equal volumes of different substances we find that there are great variations in the weights. If a certain volume of hydrogen, the lightest element, weighs 1 grain, the same volume of air weighs 14; of water, 11,943; and of osmium, the heaviest element, 267,553. There is a constant and peculiar relationship between the weight and the volume of every natural substance. This relationship is called the specific gravity. The *specific gravity* of a body is its weight, as compared with the weight of an equal bulk of a standard body taken as unity.

The *density* of that body is its *mass* or quantity, as compared with the mass of an equal volume of a standard substance. By the law of gravitation the weight or gravitative force is directly proportionate to the mass, hence no error ordinarily results from the indifferent employment of the two terms. Sometimes the term density is used to signify the specific gravity of a vapor, taking hydrogen as a unit.

Water is so easily obtained in a pure state that it is chosen as a standard for both liquids and solids; that is, the latter are said to be so much lighter or so much heavier than water. When it is said that the specific gravity of urine is 1020, it is meant that a bulk of urine equal to the bulk of 1.0 part of water will weigh

1.020 parts. Likewise we say that the specific gravity of a dry gall-stone is 0.9, meaning that equal bulks of water and the concretion bear the proportion to each other by weight of 1 and 0.9.

For **specific gravity of solids heavier than water** application is made of the principle that a substance immersed in a liquid displaces a bulk of that liquid equal to the bulk of the body immersed.

The body may be slowly submerged in the water contained in a suitable vessel filled to the brim. The overflow is caught and weighed, and the ratio calculated as follows:

Weight of water : weight of body : : 1 : specific gravity.

Thus, a piece of sulphur weighing 32 grams and held by a thread was very slowly immersed in a lipped vessel filled to the brim with water. The overflow was caught in a tared beaker, and weighed 16.5 grams. Then—

$$16.5 : 32 :: 1 : \text{specific gravity} = 1.9+.$$

A more convenient and accurate method makes use of the law: "A solid immersed in a liquid loses a weight equal to the weight of an equal volume of the liquid." The body is suspended by a fine thread or platinum wire, and weighed in the air. It is next totally immersed in pure water and its weight noted. By subtracting the weight in water from the weight in air we obtain the loss in weight, which represents the weight of an equal bulk of water. Then—

Loss in water : weight in air : : 1 : specific gravity.

For example, weight of body in air, 9.560 grams.
weight in water, 8.540 "
loss in weight, 1.02 "

$$\text{Therefore, } 1.02 : 9.56 :: 1 : \text{specific gravity} = 9.37.$$

By Rule.—*Divide the weight in air by the loss of weight in water, and the quotient is the specific gravity, with water as the unit.*

For **solids lighter than water** and which float of themselves it is necessary to add a sinker, such as a glass bead full of mercury, or a piece of lead. The body is weighed and then attached to a sinker which has been previously weighed in air and in water, and its loss noted. The two are weighed together, first in air and then

in water, to determine their joint loss. The joint loss, less the loss of sinker, gives the loss of the light body.

From this the specific gravity is determined, as above, by dividing the weight of the light body in air by the loss of weight in water. For example: a dry biliary concretion floats on water; if it be sunk by attaching to it the heavy body used in the illustration of finding the specific gravity of solids heavier than water, then—

Concretion weighs in air,	0.910	grams.
sinker weighs in air,	9.56	"
both weigh in air,	10.47	"
both weigh in water,	8.47	"
both lose in water,	2.00	"
sinker loses in water,	1.02	"
then concretion loses in water,	0.98	"

and $0.910 \div 0.98 = 0.928 =$ specific gravity of concretion.

For Powders.—After noting the weight of the powder (w) put it in a counterpoised bottle with a mark of capacity, say 50 c.c. or grams. Fill the bottle to the mark with pure water and weigh. From the joint weight subtract the weight of the powder; this will give the weight of the water, which, subtracted from the known weight of the water filling the bottle 50 grams, will leave the weight of a volume of water equal to that of the powder (w′). From these factors the specific gravity is calculated by the same rule-of-three as in previous cases:

Weight of water (w′) : weight of body (w) : : 1 : specific gravity.

For Liquids.—In the metric system the weight of 1 c.c. of water at 4° C. (39.2° F.) is called 1 gram, therefore, the weight in grams of 1 c.c. of a liquid is identical with its specific gravity.

When the sample to be tested is small in amount, a rapid computation can be made by weighing, in grams, the liquid in a glass pipet holding 1 c.c. when filled to the mark (Fig. 1). The liquid is drawn up above the scratched ring on the neck by suction with the mouth or with a rubber medicine-dropper. The excess is permitted to drop out until the level of the ring is reached. Then, having detached the rubber tube and wiped the glass dry, the pipet and contents are weighed in a horizontal position on a wire rack or on the scale-pan. A counterpoise or *tare* should be made in advance, to cancel the weight of the empty pipet and rack. As stated above, the weight of the liquid will be its specific gravity.

The process is convenient and the liability of error is less than 0.001. When larger quantities are dealt with the result is even more accurate.

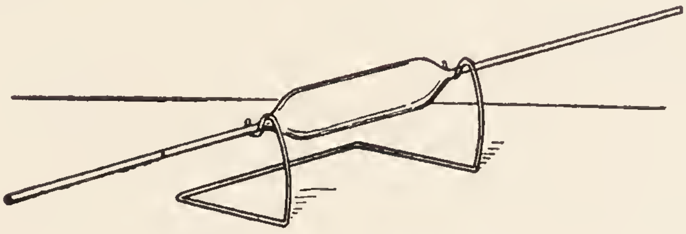


FIG. 1.—Specific gravity pipet.

The weight of a liter (1000 c.c.) in kilograms (1000 grams), or the weight of 50 c.c. in grams multiplied by 20 (= 1000 c.c. in kilograms) is the specific gravity of the liquid. To take the specific gravity by this method a *pyknometer* (Fig. 2) or *specific-gravity bottle* is used. This bottle has a narrow neck and may be obtained small enough to contain 5 or 50 c.c., or perhaps fully 1000 grains of water, or, in fact, any known quantity capable of being weighed on a delicate

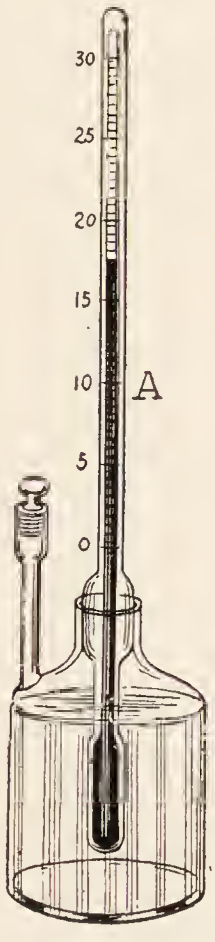


FIG. 2.—Pyknometer: A, Thermometer in neck of bottle.

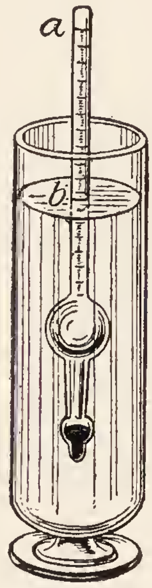


FIG. 3.—Hydrometer.

balance. An accurate tare for the empty bottle is placed in the opposite scale-pan. The bottle is filled to the mark or perhaps to the brim with the liquid, and wiped dry on the outside. It is then carefully weighed. If it be a 1000-grain bottle the weight in grains will at once stand for specific gravity with water as 1000. A rule-of-three sum will be needed if the capacity is other than 1000, as—

Known capacity : weight of liquid : : 1 : specific gravity.

In careful observations it is necessary to make allowance for variations of temperature, which by expanding or contracting the fluid will alter its specific relationship to an equal bulk of water at 15.5° C. (60° F.), the standard point. By the use of ice in a surrounding vessel the temperature of the fluid can be held at 15.5° C. (60° F.) while under examination. With simple liquids calculation with a factor of error for variation may be used. For the urine a rough allowance is made of 1 degree of specific gravity on the hydrometer scale for each 3° C. (5.4° F.) of temperature above or below the temperature at which the hydrometer or urinometer was standardized. Thus the specific gravity of a sample of urine was 1025 when the room temperature was 21.5° C. (71° F.) as 21.5° is 6° higher than the standard, we must add 2 degrees of specific gravity to the 1025, making 1027. If the room temperature was lower than 15.5° C. the difference must be subtracted according to the same allowance. On the continent of Europe the point of maximum density of water, 4° C. (39.2°), is chosen for comparison. The tables of the U. S. Pharmacopœia are based upon a standard temperature of 25° C. (77° F.) which was adopted because the average temperature of laboratories in the United States is 77° F.

Hydrometer.—Though not quite so accurate in its results as the method by the pyknometer, that by the *hydrometer* (Fig. 3) has the commendations of being very easy and ready, and of dispensing with weights and balance. It is therefore commonly resorted to in medicine, pharmacy, and the other arts. The hydrometer is a spindle-shaped glass instrument, having a graduated stem above and a weighted bulb below, intended to float upright and measure the volume of liquid displaced. The zero of the graduated scale is the point (*a*) to which the instrument sinks in pure water, and may stand for 1000 or for 1.000. Degrees above and below this point indicate the specific gravity of the liquid, the surface level of which makes a line coinciding with the mark (*b*) on the upright scale of the floating instrument. Special scales are made for use in the arts by which the strength of aqueous solutions, or the percentage of alcohol in various spirits may be expeditiously determined. These, according to their purpose, are styled *lactometer*, *urinometer*, *saccharometer*, *alcoholometer*, etc.

Physicians frequently use the urinometer to determine the amount of "solid urine" dissolved, and also to get a clue as to the presence of albumin or sugar. Its various applications are discussed on pages 583, 597. The scale of the urinometer is marked for liquids heavier than water, and usually ranges from zero or 1000 at the top to 60, meaning 1060, at the bottom. In practising

this method the glass cylindric vessel which usually accompanies it should be about two-thirds full of urine and the urinometer gently immersed to about 1020 and then allowed to come to a stand. If the vessel has a perfectly flat rim, it may be slowly filled to the brim with urine and then the reading made with the eye on a level. In this way the most trustworthy register can be taken.

For **gases** the specific gravity is determined in the same manner as for liquids by the pyknometer. A glass vessel of known air capacity is exhausted by the air-pump, counterpoised, filled with the gas, and weighed. Air is taken as a standard, and the calculation for comparing the weights of equal volumes of air and gas is on the same principle as that given for liquids.

For **vapor density** a series of very delicate operations is required, which, while they have no medical interest, yet are of great importance in determining molecular weights. Vapors are gases that condense to liquids or solids at ordinary temperatures. According to the method of Dumas a small glass flask, with a capillary opening in its narrow neck, is first weighed full of air. The flask is then warmed and its neck dipped into a fluid, some of which enters as the contained air cools and contracts.

In a bath of oil or mercury heated above the boiling-point the substance vaporizes, displacing the air. The neck is sealed with the blowpipe and when cool weighed. In order to find the weight of the empty vessel the point is broken with the neck under mercury. The mercury rushes in, replacing the vapor, and filling the flask. By measuring this mercury the capacity of the flask is ascertained. Then the weight of this much air at the same temperature and barometric pressure, subtracted from the original weight of the vessel full of air, gives the weight of the empty flask. This weight, subtracted from the weight of the flask full of vapor, gives the weight of the known volume of the vapor at the temperature and atmospheric pressure at which the flask was sealed. Then—Weight of air : weight of vapor : : 1 : vapor density.

HEAT

THERMOMETRY

The temperature of substances involved in chemical reactions is almost as important as their weight, for the chemical properties and behavior of bodies vary greatly with their temperature. In clinical observation of disease the temperature of the patient should never be overlooked. The presence or absence of fever is always noted most accurately by the temperature. Indeed, it has been said that the study of fever is mainly a study of temperature. The sensation of heat or cold imparted to the hand is an unsafe guide. It depends upon the state of the hand, and this varies greatly in different persons and at different times in the same person. The hand may have been chilled by recent immersion in cold water or exposure to cold air, or by temporary sluggishness of the circulation of the blood. On the contrary, it may be warmer than usual by recent immersion in warm water, or by the protection of gloves, or by exposure to the air of a warm room.

A hot body, besides communicating to the observer the sensation of *heat*, which is relative, imparts to other bodies in contact or near relation to it an *increase* in size which is constant. In general, as bodies get hotter they expand; as they cool, they contract. This physical change is objective, constant, and independent of the condition of the observer. By resort to thermometers measuring the degree of expansion we get the standard desired.

The degree of expansion determines the *state of aggregation;* that is, whether it be a solid, a liquid, or a vapor. Water below 0° C. (32° F.) is solid (ice); between 0° C. (32° F.) and 100° C. (212° F.) it is liquid; and above 100° C. (212° F.) it is a vapor (steam). By cold and pressure all gases have been liquefied and solidified.

The **molecular theory** ascribes this threefold state to variations in the range and energy of motion of the extremely minute particles of which all bodies are composed. These particles, called *molecules* (little masses), are supposed to be always in vibration. Their diameter has been calculated to be between $\frac{1}{250}$ millionth and $\frac{1}{500}$ millionth of an inch. In a solid body, though still in agitation, they are supposed to be held in a certain compact relation to one another by the operation of an attractive force called *cohesion.*

Cohesion is commonly defined as an attraction between molecules exerted at extremely small distances and manifested most strongly in solids, less in liquids, and not at all in gases. In

solids this resistance to separating forces is very great and its phases are distinguished as *hardness*, *brittleness*, *malleability*, *ductility*, and *tenacity*. The effect of heat is to antagonize cohesion, giving a wider sweep to the motion of the molecules, thus causing *expansion*. This phenomenon may be shown with a brass ball having a close-fitting ring gauge. When heated by a lamp it is found too large for the gauge, but plunged in cold water it contracts and slips through the ring easily.

In the liquid state the molecules are more free to move, though still somewhat under the sway of cohesion. A small mass of liquid mercury rounds up into a globule by virtue of this phenomenon of cohesion. This same property of holding together enables one to blow a soap-bubble to a thin film. The greater freedom of the molecules in a liquid permits them to separate further than they do in a solid by equal increments of heat. The amount of expansion in a solid is relatively small for the ordinary range of temperature.

When heated from the freezing-point to the boiling-point of water, iron expands only $\frac{1}{282}$ of its bulk; brass only $\frac{1}{179}$; but alcohol increases $\frac{1}{9}$, water $\frac{1}{20}$, and mercury $\frac{1}{55}$.

The **kinetic theory** is based upon the observation that 1 c.c. of a gas has 21 trillions of molecules. All those of a kind are alike in weight and structure. Their weight, size, rate of motion, and free path have been mathematically determined. In the air at 0° C. (32° F.) the average speed is 1591 feet, in hydrogen 6050 feet per second.

The temperature is another expression for the *kinetic energy* or rate of motion. In a second each hydrogen molecule collides 9480 million times with one of its neighbors, and the two rebound, moving 0.0001855 mm. before striking others. The water vapor molecule has a diameter of 0.00000044 mm. and a free path of 0.00000649 mm.

This free path gives the diameter of the space between the molecules.

"If we could see them we should be reminded of the dance of a swarm of house-flies in the summer air, darting about, touching one another, and then sharply darting away in a new direction. This agitation is independent of winds or any current. In calm air, though all are in motion, as many go in any one direction as in any other, and the effect is evenly balanced. In a wind more molecules move in the direction of the wind than in any other. The molecules are not aimed at one another, and as a collision is all a matter of chance the same molecule is sometimes nearly stopped, sometimes hurried, and sometimes merely deflected. The great majority, however, move with about the average speed of

the whole crowd. *Gas* is a word for a crowd of free molecules, as *nation* is a word for a crowd of men."

According to this theory the *pressure* of a gas or vapor is the cannonade of millions of molecules against the side of the vessel containing the gas. As the number of impacts per square inch and per second is enormous, the effect is indistinguishable from that of continuous pressure.

There comes a point in the expansion of a liquid when its molecules are given such a swing as to pass out of the limited range of liquid cohesion into the free state of vapor. As stated above, they are supposed now to be in rapid and incessant motion, shooting about in straight paths against one another and creating a certain pressure on the walls of the containing vessel. This is known as *vapor tension.* Gases expand relatively far more than do solids or liquids by equal increments of heat. The molecular activities of all gases are so much alike that they expand with little or no differences among themselves. Certainly in ordinary observation the rate of expansion of air, of hydrogen, of nitrogen, of carbon dioxid, and of most other gases, is about the same (*Charles'* or *Gay-Lussac's law*), being $\frac{1}{273}$ part of their volume at 0° C. (32° F.) for every increase of 1° C. ($\frac{1}{491}$ for 1° F.).[1] The total expansion in being heated through the 100° C. (180° F.) from 0° C. (32° F.) is more than one-third their bulk. For this reason *thermoscopes*, which measure the variations in bulk of vapors, are extremely sensitive and are often used for precise observations of minor changes within a short range. Any substance which expands uniformly, and whose alterations of volume under heat can be measured, will serve for a thermometer. Mercury has advantages which commend it to universal use. It can easily be procured of standard purity; it expands uniformly and with a relatively high rate for a liquid; it has the conductivity of a metal, readily settling by loss or gain to the temperature of contiguous bodies. It has a range of 389° C. (700° F.) between its freezing- and its boiling-point. Temperatures below −39.4° C. (−38.9° F.), the freezing-point of mercury, are taken with colored alcohol. Above 350° C. (662° F.), where mercury boils, the air pyrometer is used, and below —240° C., the thermopile (p. 32).

[1] *Correction of Volume for Temperature.*—The decimal corresponding to $\frac{1}{273}$ is 0.003665, which is called the *co-efficient of expansion of gases.* When heated from 0° C. (32° F.) to 1° C. (33.8° F.) one volume of air or of nitrogen becomes 1.003665 volumes; at 2° C. (35.6° F.) it would be increased by double the *co-efficient* (0.003665 × 2°) = 0.00733. If the temperature be above 0° C. (32° F.), in order to correct the observation by reduction to the standard 0°, the observed volume is divided by the factor [1+(0.003665×observed temperature)]. Thus, the volume of nitrogen in an urea apparatus was 60 c.c., the temperature of the room was 20° C. (68° F.), what would be the volume at 0° C. (32° F.)? Answer: 1+(0.003665 ×20°)=1.07330. Then 60÷1.0733=55.90 c.c.

The Mercurial Thermometer.—A thermometer of precision ought to be made of a selected tube which is carefully divided into parts of equal volume of the bore (Fig. 4). Two fixed points are marked as standard: the point reached by the mercury when the instrument is embedded in melting ice, the *freezing-point* and another point higher up reached when exposed to steam at average atmospheric pressure, the *boiling-point.* The freezing-point on the Centigrade scale is marked zero (0°); between it and the boiling-point one hundred degrees are marked. On Fahrenheit's scale the freezing-point is called 32° and the boiling-point 212°, there being 180° between them. In Réaumur's scale the freezing-point is marked 0°, but the boiling-point is 80°. In English-speaking countries both Centigrade and Fahrenheit are used, the latter almost exclusively by physicians, by the weather bureau, and in the household. In scientific circles in this country and in most countries of Europe the Centigrade is preferred. In making the scales the space covered by 100° C. includes 180° F., hence their relative values are as 1 to 1.8 or as 5 to 9. This relation is complicated by the fact that Fahrenheit's zero is not at the freezing-point, but at thirty-two of his degrees below it. To start from the same point for both we must add or subtract 32, according to circumstances. Briefly then:

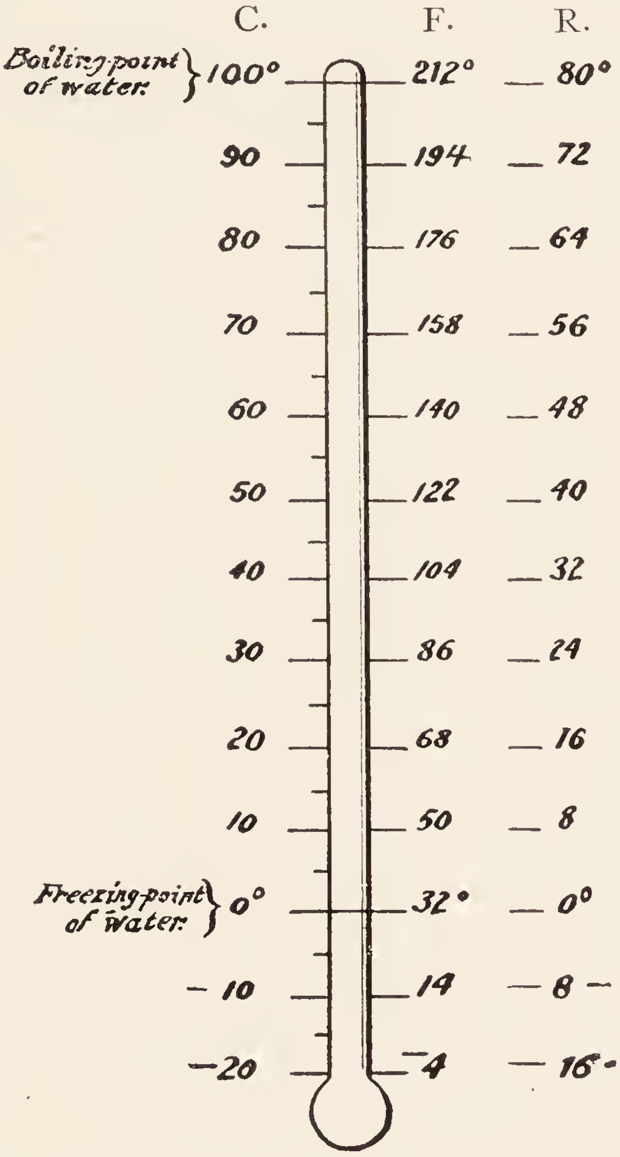


FIG. 4.—Thermometer showing Centigrade, Fahrenheit, and Réaumur scales.

To convert Centigrade above 0° to Fahrenheit, multiply by 9 and divide by 5 and add 32 to the product. To illustrate: The point when water is densest is 4° C.; what is this according to Fahrenheit?

$$4° \times 9 = 36°, \quad 36° \div 5 = 7.2°, \quad 7.2° + 32° = 39.2° \text{ F.}$$

The formula for this calculation is $F. = \frac{9}{5}\ C. + 32$.

To convert Fahrenheit into Centigrade degrees subtract 32, multiply the remainder by 5, and divide by 9. To illustrate: The

normal temperature of the human body is 98.6° F., what is this on the Centigrade scale?

$$98.6° - 32° = 66.6°, \quad 66.6° \times 5 = 333°, \quad 333° \div 9 = 37° \text{ C.}$$

The formula for the above is $C. = \frac{5}{9}(F. - 32)$.

For degrees below zero a similar calculation is used. Thus, mercury freezes at −39.4° C., what is this reduced to Fahrenheit?

$$-39.4° \times \tfrac{9}{5} = -70.9°; \text{ and } -70.9° + 32° = -38.9° \text{ F.}$$

The Absolute Zero.—As gases shrink $\frac{1}{273}$ of their volume for each degree of Centigrade ($\frac{1}{491}$ for 1° F.), it is supposed that at −273° C. (−459.4° F.) there would be no possibility of further shrinkage from loss of heat, and the molecules would be at absolute rest. This is supposed to be the temperature of interstellar space, and is called the *absolute zero.* Low temperatures are produced artificially; −258° C. (−432.4° F.) has been obtained by allowing liquid hydrogen to boil under diminished pressure. At this point, which is 15° C. (27° F.) above absolute zero, the liquid hydrogen at ordinary pressure freezes. One gas has a lower boiling- and freezing-point than hydrogen, and that is helium, which freezes at −268° C. (−450.4° F.) or 5° C. (9° F.) above the absolute zero.

At very low temperatures mercury, alcohol, and even air are frozen; hence their expansion cannot be used to measure variations of the lowest temperatures. The thermometer often used is a platinum wire in an electric circuit with a galvanometer. As the temperature falls, the resistance of the platinum falls also, and the galvanometer shows a corresponding increase of current-strength. Within 30° C. of absolute zero this method is not correct. For these lowest points a thermopile is used, of silver and platinum, with liquid oxygen as a standard, and a delicate galvanometer to detect the difference. It is believed to be accurate down to the melting-point of helium, which is 5° or 6° C. above absolute zero.

The *absolute temperature* is reckoned from the absolute zero by adding 273 to the Centigrade reading and 459 (491−32) to the Fahrenheit. Thus, hydrogen freezes at −258° C.; therefore −258° + 273° = 15° C. of absolute temperature.

The Clinical Thermometer.—The instrument used to note the variations of human temperature should not only be correct in its indications of one-fifth of a degree, but should act quickly (in from ½ to 4 minutes), should hold the register at its highest reach, even after removal from the mouth, anus, or armpit, and should

be so constructed as easily to be made aseptic. Correctness is obtained by graduating after comparison with a standard instrument at several nearly related temperatures. Sensitiveness or promptness of action is produced by having the smallest possible volume of mercury in the bulb and a fine bore in the indicating column. To make this hair-like column visible it is sometimes flattened into a ribbon and the glass shaped to act as a lens. To make an instrument self-registering, various devices have been employed by which the top of the column is held stationary while the mass of the mercury is free to contract within the bulb. The principle in common use is that of constricting the tube at some point, so that the impediment will arrest the downward motion of the mercury above it and break the column. In the best form of thermometer the mercury must pass by an extremely narrow channel around the sharp corner of a piece of glass sealed into the bore. When warmed the expanding mercury is forced past this obstruction, but on cooling, the portion which has been driven above remains stationary while the lower portion contracts, thus making a gap in the column. This stationary portion indicates the maximum temperature.

To set the instrument for taking an observation the top of this detached column must be lowered to the point of 35° C. (95° F.). This is done by mechanical means, but jarring and striking the instrument sometimes causes it to slip out of the hand, to be broken on the floor. Centrifugal force serves us best and is brought into play by holding the tube firmly with the bulb end downward and swinging it briskly or throwing the hand forward and jerking it back quickly, as in cracking a whip.

It is necessary for accuracy that the instrument should not be graduated until the glass is seasoned. The tube is not always uniform in its caliber. It may be correct at 35° C. (95° F.), but incorrect at 38° C. (100.4° F.).

On these accounts it has become customary for dealers to furnish certificates of correctness which attest accuracy or give the factor of error for several points on the scale. For clinical purposes, where it is frequently necessary to make an instrument aseptic, the glass tube with the scale engraved upon it is to be preferred to any form using metal or any other material. The smooth and rounded surface is least likely to harbor infectious germs, and it can be easily sterilized by immersion in any antiseptic fluid such as formaldehyd, alcohol, or solution of cresol.

The range of human temperature being limited, the scale of the clinical thermometer needs to be but a few inches in length. It should register variations of one-fifth of a degree from 33.3° C. (92° F.) to 43.3° C. (110° F.), and have marked upon the glass the

3

minimum time of exposure required for it to reach the true temperature. The normal temperature is 37° C. (98.6° F.). A rise of more than one degree means that the patient is feverish. Long-continued temperature above 40.5° C. (105° F.) is dangerous because it induces widespread degenerative changes in the body.

Clinical Temperatures

Above	105.8° F.	or 41° C.	Hyperpyrexia.
Between	104° and 105° F.	or 40° and 40.5° C. . . .	High fever.
"	102° and 103° F.	or 38.8° and 39.4° C. . . .	Moderate fever.
"	99.5° and 101.5° F.	or 37.5° and 38.6° C. . . .	Slight fever.
Normal	98.6° F.	or 37° C.	Health.
About	97.7° F.	or 36.5° C.	Subnormal.
Below	97° F.	or 36° C.	Collapse.

SPECIFIC HEAT

The thermometer is used to mark the intensity with which heat acts, but it is necessary to supplement its reading with other observations if we would learn the quantity of heat engaged. An elevation of temperature of 1° in a given quantity of water requires that a certain amount of heat should be supplied to the water; to raise another equal mass of water through 1° requires an equal amount of heat. It follows, therefore, that twice the amount of water in rising through 1° will absorb twice the amount of heat as was needed for the single mass. This gives us a unit for recording the quantity of heat—"the amount required to raise one gram of water one degree Centigrade in temperature." It is called the *gram-degree* unit of heat, or the *calorie*, and is abbreviated *cal.*

For stating large transfers of heat, as in dealing with the fuel value of foods, it is desirable to have a large unit. The *large Calorie* (*Cal.*) is the amount of heat required to raise one kilogram of water one degree Centigrade or about 1 pound of water 4 degrees Fahrenheit. It is equal to 1000 *small calories* (*cal.*).

Heat Capacity.—To raise the temperature of equal masses of different substances, such as copper, mercury, or lead, through the same number of degrees, different quantities of heat are absorbed. This heat reappears when the bodies return to their original temperature. Each body is thus shown to have a different *capacity* for absorbing heat. The *thermal capacity* of water is the heat that must be supplied to it to *raise one gram through one degree Centigrade.*

In a suitable instrument known as a *calorimeter* the capacity for heat of any body can be compared with that for water. This gives us the *specific heat* of the body, which is *the ratio between its heat capacity and that of water taken as* 1. When equal weights

of mercury and water are exposed to the same heat for the same period it is found that while the water rises 1° C., the mercury will rise 30° C. Therefore, the thermal capacity of mercury is $\frac{1}{30}$ or 0.0333 that of water—that is, the specific heat of mercury (water = 1) is 0.0333.

A study of heat capacity is of great importance to the chemist, as it serves for the calculation of atomic weight. The specific heat of solid elements is inversely proportional to the atomic weight; hence, for solid elements the product of the two is a constant quantity. As stated by Dulong and Petit: "The solid elements have the same atomic heat." The constant product averages 6.4. It follows, therefore, that knowing the specific heat of a solid, we can determine the atomic weight by dividing 6.4 by the specific heat.

MELTING AND FREEZING

The temperature of a solid rises by the application of heat until it reaches the *melting-* or *fusing-point*, when a physical change occurs, the body becoming a liquid. This change depends upon a play of molecular energy which is definite for any given substance at a given temperature. It therefore takes place at a fixed point for each substance, and is a constant characteristic for every substance which is not altered chemically by the action of heat. No means of identifying substances and testing their purity is more often used than that of the determination of the melting-point. When pure, a substance always melts exactly at this point. Should a part of it melt at this degree and the other part remain solid up to a higher temperature, thus rendering an indefinite report, it is evident that we are dealing with a mixture and not the pure substance.

A sharply accurate melting indicates great purity, for the least impurity causes a considerable change in the melting-point. The following are the melting-points of a few substances: mercury, −39.4° C. (−39° F.); carbolic acid, 35° C. (95° F.); potassium, 62.5° C. (144.5° F.); benzoic acid, 120° C. (248° F.); salicylic acid, 155° C. (311° F.); tin, 227.8° C. (442° F.).

Determination of the Melting-point (Fig. 5).—A minute quantity of the substance is placed in a short capillary tube (*c*) closed at one end and attached to a thermometer (*d*) by small rubber bands. The thermometer carrying the substance is immersed in a beaker (*a*) containing a liquid having a high boiling-point, like concentrated sulphuric acid. Heat is applied gradually and the acid constantly stirred with a glass stirrer (*b*) until the solid is seen to liquefy. The thermometer reading is then taken as the melting-point (m.-p.) of the solid. Freezing or solidification

of the liquid occurs at a point practically identical with the melting of the same substance in its solid state.

Latent Heat.—When the amount of the solid is considerable, much time is consumed in melting, and the thermometer does not rise during the whole period of transition from the solid to the liquid states, although much heat is being applied. The heat so absorbed and unrecorded by the thermometer is called *latent;* because it appears to be stored up and hidden, to reappear as *sensible* or *free* heat in equal amount when the liquid freezes. Strictly speaking, it is no longer that form of molecular vibration recognizable as heat, but is the energy employed in overcoming molecular cohesion and in maintaining the molecules in their new relative positions.

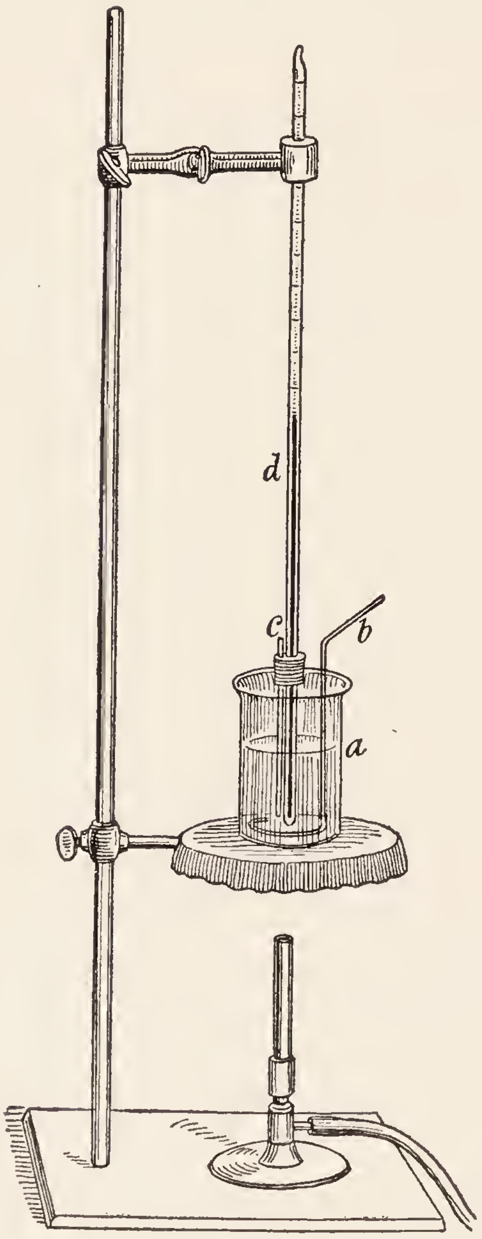


Fig. 5.—Determination of melting-point.

The amount of heat that disappears varies with the material substance and its mass. Like the melting-point, it is definite and characteristic for each individual substance.

Specific heat of fusion is the number of *calories* (heat units) required to change one gram of a substance from the solid state to the liquid, the temperature remaining constant.

If a kilogram of water at 0° C. is mixed with an equal weight of water at 100° C. there will be two kilograms at 50° C. If a kilogram of *ice* at 0° be mixed with a kilogram of water at 100° C., the melted mixture will have a temperature of only 10.4° C. In this last experiment each gram weight of water at 100° C. in cooling to 10.4° C. will have given off $100 - 10.4 = 89.6$ calories. In losing this 89.6 calories it has melted one gram of ice and warmed up the resulting water 10.4° C., which equals 10.4 calories. Subtracting this from the 89.6 calories gives us $89.6 - 10.4 = 79.2$ calories. In melting one gram of ice at 0° C. there disappeared or was made *latent* enough heat to raise the temperature of a gram of water 79.2° C. The molecules have used up this energy in acquiring a freedom of movement among themselves not previously possible while cohesion held them in the stable position characteristic of solids. To

liquefy water requires 79.2 cal., a higher latent heat of fusion than any other liquid. Acetic acid requires 43.7 cal.; benzine, 29.1 cal.

Effect of Pressure on the Melting-point.—In most cases the change from the solid state to the liquid is attended by expansion. To this rule there are exceptions, such as ice, bismuth, and iron, which contract on fusion. A body that expands in fusing has its melting-point raised by pressure. The effect of pressure is so slight that a pressure of 156 atmospheres raises the melting-point of spermaceti only 3° C. (5.4° F.).

On the other hand, the bodies that contract in fusing have their melting-point lowered by pressure. For instance, with ice, pressure makes the change to water more easy. In moulding a snowball pressure without heat will melt the ice crystals, because the compressed snow has a melting-point lower than 0° C. (32° F.). On removing the pressure the ice grows hard again, uniting the crystals. This is the phenomenon termed *regelation*. The fusion-point of water is lowered only 0.0075° C. (0.0135° F.) for each atmosphere of pressure.

Reactions of the State of Equilibrium.—When we have made a mixture of ice and water at 0° C. (32° F.), in which they exist side by side unchanged, if we put pressure on it the equilibrium is disturbed. In order to relieve the pressure the ice melts, because liquid water occupies less space than the solid. The melting-point of the ice is lowered, but, on the other hand, the pressure is reduced. This is an illustration of the *law of reaction* which holds for all states of equilibrium in chemistry and physics: *When a system in equilibrium under constraint shifts its equilibrium, there is a reaction which opposes and partially destroys the constraint.* From this it is seen that an equilibrium is a more or less stable condition which, when disturbed, tends to restore itself by reversing the disturbance (p. 82).

Freezing Mixtures.—Making a solution of a solid causes a lowering of temperature. As the melting of a solid consumes heat, so does the liquefaction of a solid by a solvent. The heat is taken from the mass itself. This is the principle involved in the production of artificial cold, which may be sufficient in certain cases to produce a lowering in temperature of surrounding bodies, and thus act as a freezing mixture. The more rapid the process of liquefaction the greater is the degree of cold produced, as there is less time for heat to be conducted from without. When snow or shaved ice, two parts, is mixed with one part of common salt, it quickly liquefies and then dissolves the salt, both changes reducing the temperature of neighboring substances from 0° C. to −22° C. (−7.6° F.). A mixture of 5 parts of potassium

nitrate, 5 of ammonium chlorid, and 19 of water lowers the temperature from 10° C. (50° F.) to −12° C. (10.4° F.).

Cryoscopy.—The freezing-point of a liquid is lowered by dissolving in it any substance, solid, liquid, or gaseous. The salt water of the sea remains unfrozen when the rivers flowing into it are covered with ice. The reduction of temperature is proportionate to the amount of dissolved substance. Expressed in another way, the lowering of the freezing-point is proportionate to the number of molecules dissolved in a given volume (p. 96).

For medical studies *cryoscopy* is limited to the determination of the freezing-point of organic fluids, such as urine, milk, or blood, by means of which information is obtained regarding the amount of matter held in solution. It is based on the *law of Raoult*, that a definite quantity of any substance expressed in molecules (*i. e.*, the molecular weight of the substance in grams), dissolved in a definite quantity of fluid, lowers the freezing-point of the solvent by a constant amount. From this it follows that the lowering is dependent upon the *number* of molecules in solution, and not upon their nature, size, or material. After dissolving in 1000 c.c. of water the molecular weight of any substance in grams, we find that the freezing-point of the water is depressed 1.87° C. (3.35° F.). This is the value of its molecular lowering. In an aqueous solution the amount of depression in Centigrade degrees below the freezing-point of pure water is often expressed by the symbol Δ, *delta*. The Δ of normal blood is 0.56; that of normal urine varies from 1.2 to 2.3; that of cows' milk is 0.55 to 0.56, whether Pasteurized or not. If the freezing-point of a sample of milk is −0.52° C. (31.06° F.), then it has been manipulated. Making allowance for temporary variations, due to excessive consumption of water on the one hand, or of salt food on the other, depression in the freezing-point of the blood shows failure of the kidneys to remove the effete substances. Serious disease of the kidneys may depress it one degree below the normal.

For exact researches upon cryoscopy the apparatus commonly used for determining the melting-point of solids is not sufficiently precise. The instrument and elaborate technic of Beckmann is best.

A special differential thermometer (*T*), graduated into hundredths of a degree, is inserted into a stout glass tube (*A*) one inch in diameter, so that the bulb is ¼ of an inch from the bottom of the tube. Both of these are fitted, without touching, into a larger tube (*D*), which acts as an air-jacket.

These are supported in an upright position by a cover (*E*), placed on a glass jar of two-liters capacity. This jar is filled two-thirds with shaved ice, two parts, and salt, one part, which is enough to lower the temperature to the desired point, about −5° C.

(23° F.), taken on an ordinary thermometer. The liquid to be examined is poured into (*A*) by the side tube (*B*), and in sufficient quantity to cover the bulb of the special thermometer; then (*A*) is placed into the larger tube (*D*), which serves as a cool chamber.

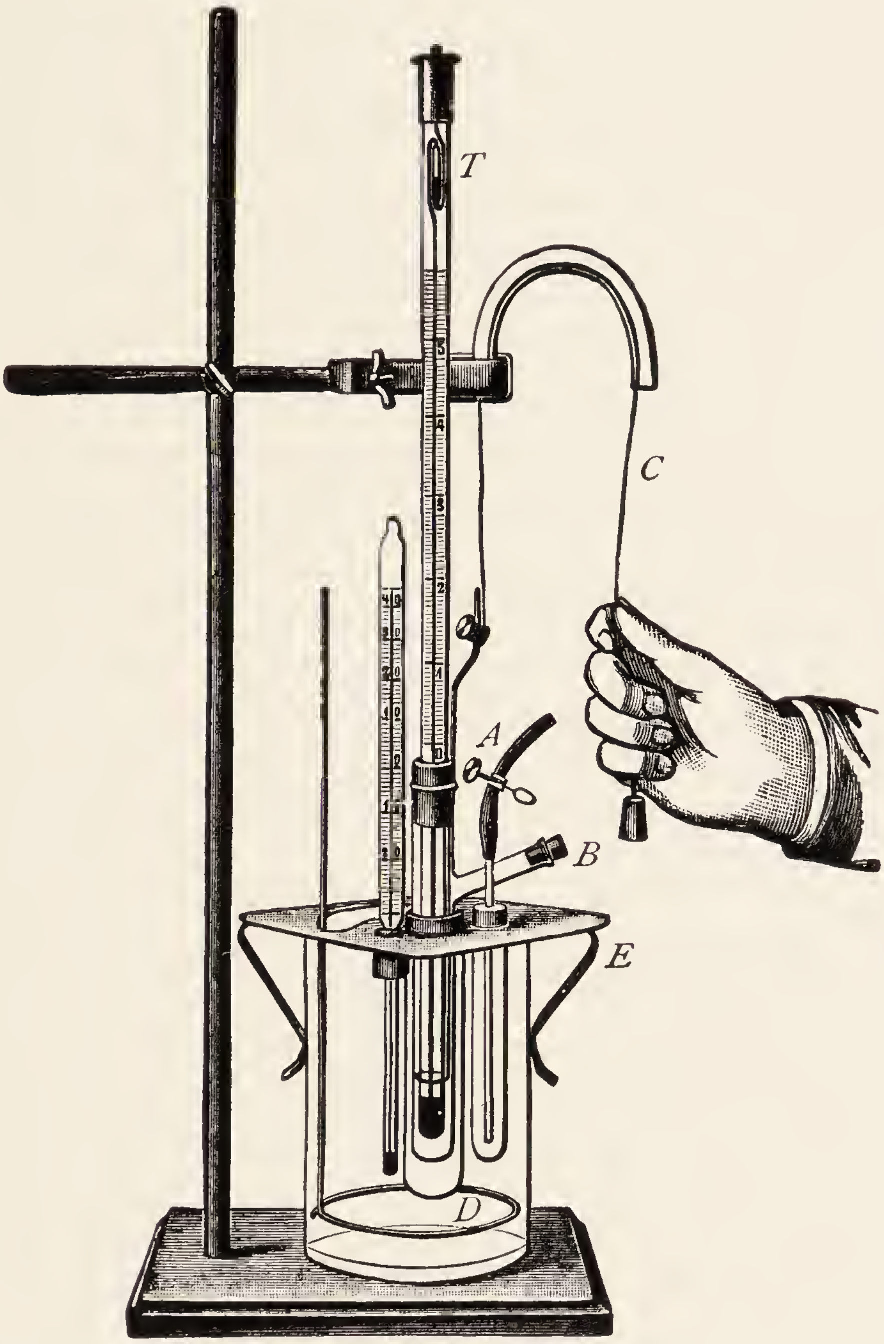


Fig. 6.—Cryoscopic apparatus.

The liquid is stirred by the wire (*C*). In about ten minutes the liquid becomes a thick slush; then the freezing-point is read, as differentiated from that of pure water, which has been before determined and recorded. Duplicate determinations may be taken to insure accuracy.

EVAPORATION

A liquid exposed to the air dries up—that is, passes into the state of invisible vapor or gas. This *spontaneous evaporation* occurs slowly at all temperatures, but when the liquid is boiled the process is much more rapid. It has been stated before that the molecules of a liquid have some freedom of motion. This motion is sufficient to carry those that have reached the free sur-

face, with some velocity, beyond the limit of the liquid into the air. No longer under the sway of the cohesive force that held the molecules in the liquid state, they now move freely in all directions in straight paths, some striking others and rebounding, but all tending outward.

In a confined space the evaporation appears to cease very soon, but in reality it continues, the movement being reciprocated, for as many rebound to the liquid as leave its surface. When there is an equilibrium between evaporation and condensation the air-space is said to be *saturated* with vapor.

If a few drops of a liquid are permitted to rise through the mercury in a barometer tube, as soon as they reach the surface they evaporate and the mercury falls. The vapor exerts a pressure inside, which counterbalances some of the outer air-pressure that previously held the mercury at 760 mm. (30 in.). This pressure is due to the bombardment of the molecules and is called *tension*. More liquid will depress the column still further, but eventually some will remain unevaporated on top of the mercury. For that temperature the pressure has reached its maximum and the space is saturated. At a given temperature different vapors depress the column to different amounts. At 20° C. (68° F.) water vapor depresses the column 17 mm. (0.6 in.); alcohol vapor 60 mm. (3.54 in.); and ether 450 mm. (17.7 in.).

If a barometer tube has its space above the mercury saturated with vapor, and we raise the temperature about the tube, it will be seen that as the temperature rises the barometer column falls, showing increased vapor tension. The saturation pressure rises correspondingly to the rise of heat. The difference of height between an ordinary barometer and one saturated with vapor in its upper space gives the vapor tension of the substance for that temperature. The saturation vapor-pressures of water are stated in the table below:

Tension of Aqueous Vapor in Millimeters (Regnault)

Temperature.	Tension.	Temperature.	Tension.	Temperature.	Tension.
C.	mm.	C.	mm.	C.	mm.
0°	4.6	11°	9.8	21°	18.5
1	4.9	12	10.4	22	19.7
2	5.3	13	11.1	23	20.9
3	5.7	14	11.9	24	22.2
4	6.1	15	12.7	25	23.6
5	6.5	16	13.5	26	25.0
6	7.0	17	14 4	27	26.5
7	7.5	18	15.4	28	28.1
8	8.0	19	16.3	29	29.8
9	8.5	20	17.4	30	31.6
10	9.1				

If the given space be not a vacuum, but already occupied by air or other gases at the same temperature, the same quantity of aqueous or other vapor will diffuse into it. The only difference is that vaporization will go on more slowly because the liquid particles encounter resistance to their passage into the space. The highest pressure of the new vapor will be the same in the occupied space as it was in the vacuum. As each vapor exerts its own pressure unaffected by others present, it follows that the total pressure of a mixture of vapors would be equal to the sum of all the pressures—shown by each separate vapor when confined singly to the same space.

BOILING

If the table of tensions had been extended to 100° C. (212° F.), it would have stated that the pressure at that point exactly balanced a column of mercury 760 mm. or 30 in. high—that is, it was equal to the weight of the atmosphere. From this we deduce the law: that "boiling of a liquid occurs at the temperature which raises the tension of its vapor to a point equal to the pressure of the atmosphere." As soon as the tension rises beyond that point the liquid molecules are animated with such energy that those on the surface line press back the superincumbent air and fly with great velocity into the space above the liquid. The molecules below the surface form bubbles of vapor which, being specifically light, float up to the surface, burst, and scatter their contents into the air.

In consequence of the above law, decreasing the pressure on a liquid enables it to boil at a lower temperature. In the vacuum of an air-pump water will boil at the temperature of a living room. On the other hand, if the pressure be increased, the boiling-point rises. In a closed boiler water may be heated far above 100° C. (212° F.) without boiling, because its vapor is confined and presses back upon the liquid, obstructing the free passage of the molecules.

Boiling-point.—A pure liquid under the same conditions of pressure always boils at the same temperature. Like the melting-point of a solid, the boiling-point of a liquid is so constant as to be a test for purity. The usual method of determination is one which immerses the thermometer in the vapor of the boiling liquid just above the surface of the liquid. The liquid is put in a flask (*A*, Fig. 7), having a side tube in the neck (*B*) for the escape of vapor. Through the perforated stopper passes a thermometer, which, when boiling begins, is surrounded by the vapor. The heat is applied gradually until the liquid boils. As soon as the mercury of the thermometer remains constant the

boiling-point is read off. For observations of extraordinary delicacy the instrument and technique of Beckmann are used, as described on p. 370.

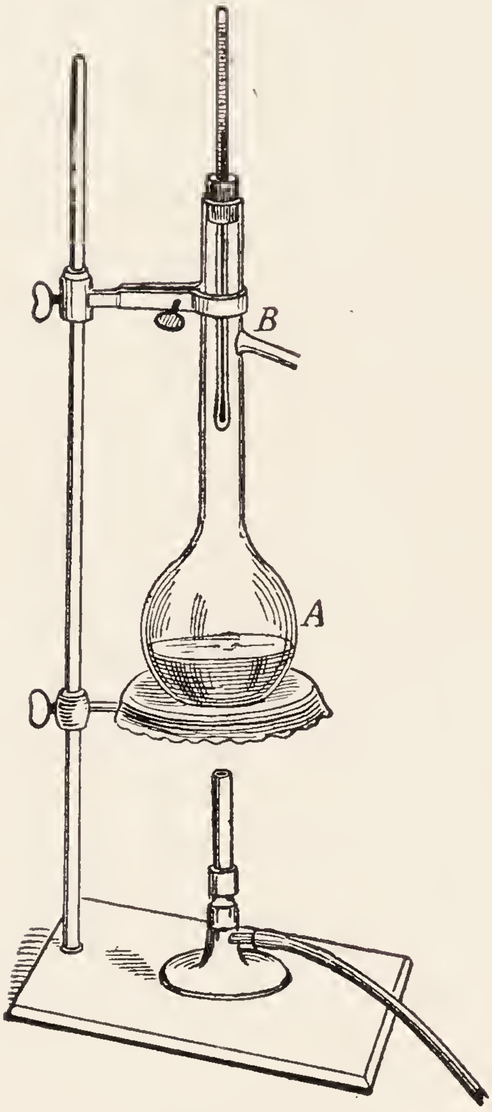


FIG. 7.—Apparatus for determining boiling-point.

Very different temperatures are required to boil different liquids. While water boils at 100° C. (212° F.), mercury requires 357° C. (675° F.), absolute alcohol, 78° C. (173° F.), pure ether, 35° C. (95° F.), chloroform, 61° C. (142° F.), oxygen the very low point −180° C. (−292° F.), and hydrogen still lower, −252° C. (−422° F.).

When a solid is dissolved in a liquid the boiling-point rises correspondingly with the concentration. Salts dissolved in water prevent its boiling at 100° C. (212° F.). The molecules of the dissolved solid, in proportion to their number, impede the escape of those of the liquid (p. 370). The diminished pressure of the atmosphere in high altitudes permits boiling to occur at a point too low for cooking in the boiler. By adding kitchen salt the boiling-point is raised sufficiently to cook the food, the effect of the altitude being canceled by the salt.

Latent Heat of Vaporization.—The spontaneous conversion of a liquid into a vapor is accomplished by absorbing heat from surrounding objects. They lose heat, hence it is said that evaporation is a cooling process. Wet clothes chill the wearer because of the evaporation of the water outside. Ether evaporates so rapidly when applied to the skin as to benumb the local sensibility through the effect of the cold produced. The absorption of heat is required to overcome the cohesion of the liquid and to impart to the particles the velocity characteristic of vapors. During the whole time of boiling away a liquid its temperature never rises above its boiling-point; all the heat not sensible to the thermometer is taken up in causing the change of molecular condition, and is called the *latent heat of the vapor.* The exact amount of heat that disappears is evolved again when the vapor is condensed. Different liquids require different amounts of heat to vaporize them. The latent heat of steam is determined in the following manner:

A kilogram of water at 0° C. is heated to 100° C. by passing

steam into it. The water now weighs 1.186 kg.—that is, to raise 1 kg. 100° C., 0.186 kg. of steam have been condensed. If 0.186 kg. of steam will raise 1 kg. of water 100° C., then 1 kg. of steam will raise 5.37 kg. of water 100° C. or 537 kg. through 1° C. Steam then has a latent heat of 537 calories, which is the highest of all vapors.

Supercooled and Superheated Water.—The exact relationship stated between the vaporous form and temperature and pressure does not obtain unless both the vapor and the liquid are present simultaneously. This appears on consideration of the following facts: Many substances in the liquid state can be cooled below their melting-point without change to the solid state. If air is excluded from the containing vessel, water can be lowered in temperature 10 degrees below 0° C. without freezing, though the peculiarity of expanding is retained. If *supercooled* only a few degrees it retains the liquid state indefinitely. At the touch of a piece of ready-formed ice it solidifies instantly, the temperature of the mass rising to the freezing-point —0° C. (32° F.). In this supercooled condition, ready to solidify by contact of ice, water is said to be *metastable.*

Suspended Boiling.—In like manner when dissolved gases have been removed by previously boiling a liquid it may be heated several degrees above its boiling-point without ebullition supervening. After water has been boiled some time in a perfectly clean vessel the phenomenon of *bumping* occurs. The dissolved air has been expelled by the first boiling, and the temperature can be raised several degrees above 100° C. (212° F.) without changing the state of the water, until at last one bubble of vapor disturbs the inertia, and a large evolution of vapor begins with sudden explosions. The water heated above its boiling-point is said to be *superheated.* This is one of the causes of boiler explosions.

Supercooled Vapor.—By excluding liquid water, aqueous vapor may retain its state even when the temperature is reduced below the point of condensation, and the vapor subjected to pressure greater than suffices for condensation ordinarily. When a receiver containing air and water is exhausted by the air-pump, the temperature declines and aqueous vapor is condensed like a fog. The same experiment performed after twenty-four hours of standing shows no mist. The particles floating in the air of the receiver have settled down and the *supercooled vapor* finds no points around which to condense.

Equilibrium of Three Phases.—There is some pressure or *vapor tension* caused by evaporation from ice, though it is but little; that from water is greater, that of warm vapor greatest, of the three forms. If accurate observations of these tensions be recorded by measured lines—upright ones for pressure and hori-

zontal ones for temperature—then curves drawn through the meeting points give the diagram (Fig. 8) for a system in which the three phases—ice, water, and vapor—exist side by side. The upright line (p) represents the height of pressure of water-vapor and the horizontal line (t) the temperature. For every temperature, a definite pressure can be found at which liquid and vapor exist unchanged.

By experiment we learn that the temperature-pressure conditions of equilibrium between ice, water, and aqueous vapor can be represented in the curves radiating from O. The two vapor pressures of ice and water intersect at the melting-point 0° C. At lower pressures than 4.6 mm. barometer, there is the field of *sublimation* of solid ice to water vapor without liquefaction. Its points are shown in the line BO. At higher temperature and pressure there is the area of *distillation* of the liquid to vapor and the boiling-points follow the line OA.

These diagrammatic curves (OA, OB, and OC) form the boundaries of three areas, *I, II, III.* The component water exists as the phase solid (ice) at any point of pressure and temperature included in area *I;* as liquid in area *II;* as vapor in area *III.* In these different areas there is a stable region for the phase common to the two curves bounding it. When supercooled water is in a state of suspended solidification, this condition of *metastable equilibrium* is represented by the curve OA'.

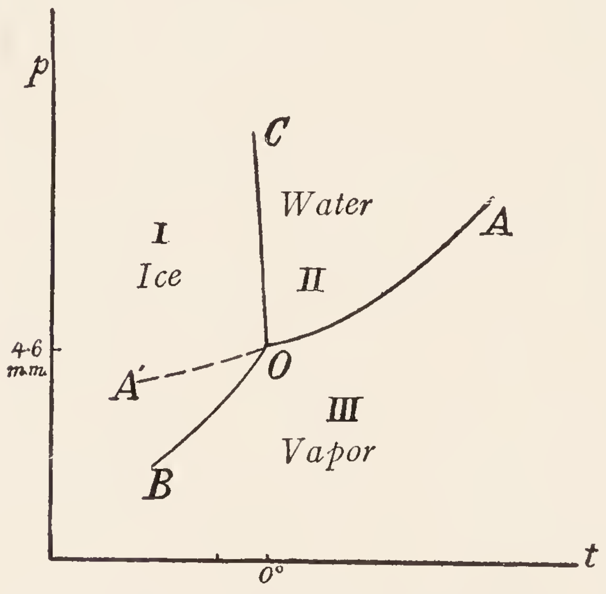


Fig. 8.—Temperature-pressure diagram of water.

The Triple Point.—At the point O the three phases exist side by side unchanged, hence it is called the *triple point of equilibrium.* Any change in pressure or temperature causes the disappearance of one phase. Increase the pressure and the vapor condenses to water, lower it and the water vaporizes. Raise the temperature and the ice liquefies, lower it and the water solidifies. In Fig. 8 the three curves run out from O to definite points well within the limits of the diagram. Thus, the abrupt terminal, A, expresses the well-known fact that there is a *critical temperature,* above which water can no longer exist as liquid. This extremity of OA shows also the *critical pressure* at which the two phases, water and vapor, disappear in the one phase—vapor. Certain chemical reactions involving several components may balance at an equilibrium like that of the triple point O (pp. 82, 134).

MAGNETISM AND ELECTRICITY

THE GALVANIC CURRENT

Lodestone or *leadstone* is the name applied to a piece of magnetic iron oxid, Fe_3O_4, because when suspended it leads or points to the poles of the earth. This natural magnet attracts iron, and if rubbed on steel bars or needles imparts to them its property of pointing north and south. The end that points north is called the south pole of the magnet, and that which points south, the north pole of the magnet. Such a magnet, dipped into iron filings, will carry away at its polar ends a quantity of the filings, bristling like a brush. If the north pole of one magnet be brought near to the north pole of another that is freely suspended, the latter will move away. The south pole, however, will be drawn to it. In the same way the south pole repels the south pole, but attracts the north.

The law of magnetic poles is that *like poles repel, and unlike poles attract.*

The earth is a great magnet, having a field of influence covering its entire surface, so that a magnetic compass at any place will show by its direction the situation of the poles that attract it.

The Galvanic Cell.—If plates of two dissimilar substances, like copper and zinc, or carbon and zinc, are immersed in an acid or other fluid which corrodes one of them, at the outside ends there will appear manifestations of energy. If the ends of the plates are connected by a wire, a succession of effects will be observed as though a continuous current of electric force was flowing through it. For instance: A magnetic needle placed near the plates tends to take a position at right angles to them just as long as they are connected by the wire, but no longer. If a solution be made a part of the circuit by immersing the ends of the wires, then chemical decomposition ensues. Chemical action upon the zinc plate transmits electricity from that plate through the liquid to the other plate which is not corroded, thereby generating a state of energy. It is similar to raising the level of a reservoir of water connected by a pipe with another one on a lower level. This phenomenon is called a *difference of potential*

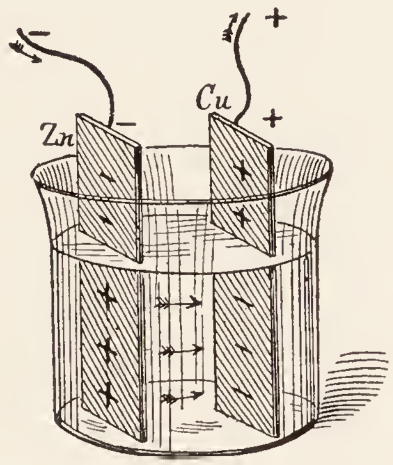


Fig. 9.—Voltaic cell of copper (*Cu*) and zinc (*Zn*) immersed in sulphuric acid, showing direction of the current.

between the plates which, when the wire outside connects them, becomes a current capable of manifesting active energy, just as the stream flowing from a higher to a lower level may do many kinds of work on the way.

As the action on the zinc plate originates the current, that plate has the higher potential. It is called *positive*, +; but the outside end or wire, called its *pole*, is electrically opposite and is said to be *negative*, −. The other plate (copper, carbon, or other substance) of lower potential is negative, −; and its pole is positive, +.

The power that initiates this transfer of electricity or difference of potential is called *electromotive force* (E. M. F.). As a difference of level in a water-system causes a corresponding pressure, so a difference of potential causes pressure or *voltage* in proportion to that difference. According to the *electronic* theory, a body excited by negative electricity is considered to have a charge of excessively minute *electrons* detached from the molecules by chemical or physical action. A body is positively electrified when it has lost electrons, and negatively electrified when it has gained them. The gain in electrons at the excited zinc end of a battery starts a transfer of them through the cell to the carbon end, which is relatively deficient. This movement of electrons along the conductor, from one molecule to the next, is something like the "handing on" of water by a line of bucket holders from the well or pond to a house afire.

The outer polar wires, being the means for the transmission of the current, are called *electrodes*. The positive pole of the copper plate is termed the *anode* from the greek prefix *an*-, up, the current moving from it up stream; while the negative pole coming from the zinc plate bears the name *cathode*, from the prefix *cath*-, down, the current moving to it down-stream. When the connections outside are continuous the circuit is *closed;* if they are broken, it is *open*. When the current is interrupted intentionally it is said to be *made and broken*. Copper wire is commonly used for connection because, like all metals, it is a good *conductor*. The glass of the cell prevents the current passing out by the bottom or sides because glass is an *insulator* or *non-conductor*, like dry wood, vulcanite, mica, and asbestos. Even the best conductors offer some *resistance* to the current, as does a conduit to the stream flowing through it.

To overcome resistance the impelling force must be increased. In the cell this is done by choosing two plates of high difference of potential. Carbon and zinc, when coupled, have a higher relative intensity than copper and zinc, which soon lose what little they had at the start. Close examination of the copper

plate shows that bubbles of hydrogen collect on it, converting the surface into one of hydrogen and not of copper.

Zn	+	H_2SO_4	=	$ZnSO_4$	+	H_2
Zinc.		Sulphuric acid.		Zinc sulphate.		Free hydrogen.

The difference of potential is lowered, unless the hydrogen is removed as fast as it forms. This is accomplished in a different way in each of the various cells that have been devised, such as Daniell's, Bunsen's, Groves', the silver chlorid, and the dry cells. The two cells most frequently used in laboratories and by physicians are the bichromate and the Leclanché.

The **bichromate (or Grenet) cell** is composed of carbon and zinc, excited by a fluid made by dissolving two ounces of potassium bichromate in a pint of hot water, and adding, when cold, two drams of mercury bisulphate and three fluid-ounces of commercial sulphuric acid. It furnishes a great quantity of current in little space and can be arranged so that the zincs may be plunged into the acid as the electricity is required. The carbon is indestructible.

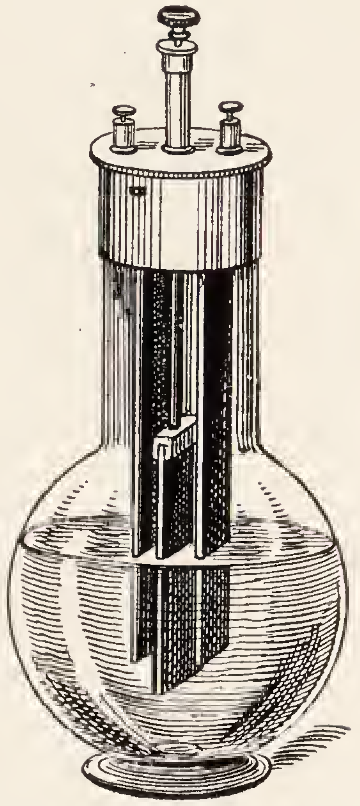


Fig. 10.—Grenet cell of carbon and zinc in bichromate fluid.

This solution forms a compound with the hydrogen, preventing the coating on the carbon plate which *polarizes* it.

The **Leclanchè cell** has several modifications, one of which is called the *carbon-cylinder open-circuit battery*. In each there is a zinc rod coupled with a compressed cylinder of carbon and manganese dioxid. The exciting fluid is ammonium chlorid, which acts on the zinc, forming a zinc-ammonium chlorid, while the hydrogen is oxidized and removed by the manganese dioxid. This battery, though not well adapted for continuous work because it polarizes rapidly, is of use for short periods intermittently. It quickly regains its strength; when left to itself it is rapidly depolarized, and thus maintains its intermittent powers for a long time without needing attention. The electromotive force from one cell is 1.5 volts only, but it can be raised to a higher degree by linking a number of cells in a series —the carbon of one connected with the zinc of the next.

A combination or battery of six cells has six times the E. M. F. of one cell, though there is an increase of internal resistance of 0.7 of an ohm for each cell.

Dry Cells.—The principle of the Leclanché cell is used in the construction of the ordinary dry cell, which has about 1.5 volts,

27 ampères, and internal resistance of 0.54 of an ohm. Instead of a glass cell, one of zinc is used, its internal surface being the positive plate; the external surface is varnished. In this cell is a

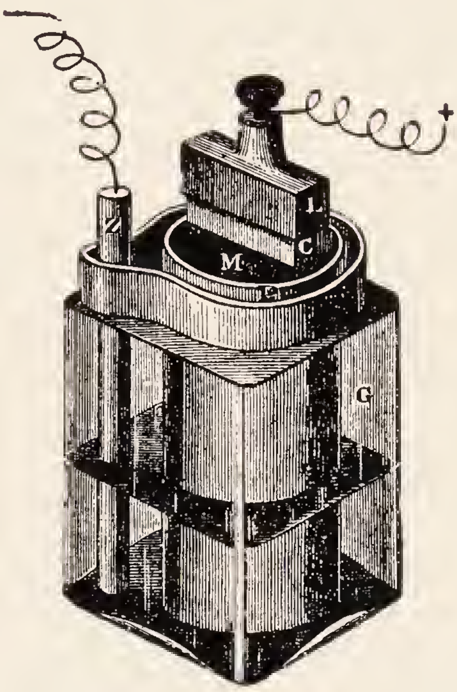


Fig. 11.—Disque Leclanché cell.

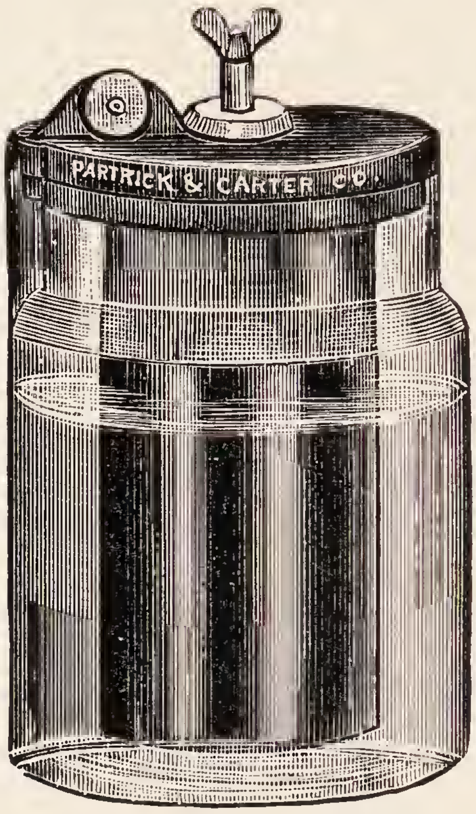


Fig. 12.—Carbon-cylinder battery.

pasty mixture of ammonium chlorid, plaster, and zinc chlorid. In the center is the carbon plate surrounded by granulated carbon and manganese dioxid, with a porous septum separating them from the ammonium chlorid. Just enough water is added barely

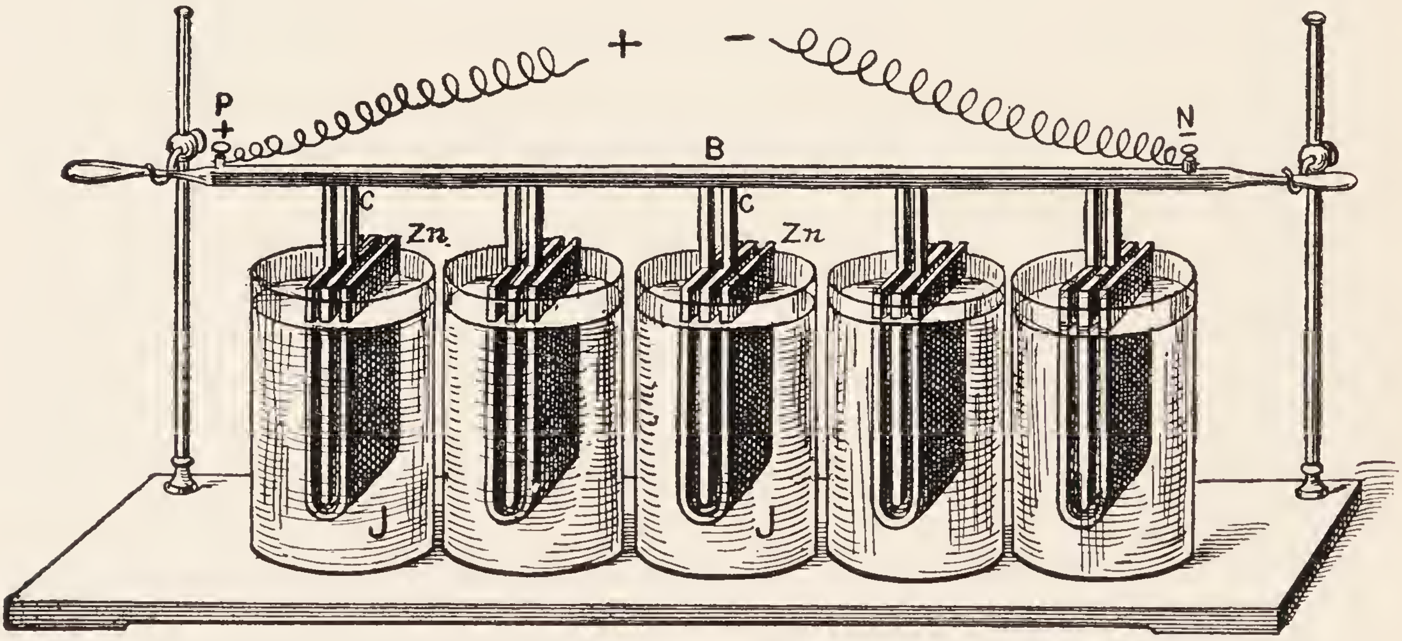


Fig. 13.—Plunge battery of carbon and zinc.

to moisten the granulated carbon, and the top is then hermetically sealed with wax. The plaster hardens and makes a compact, almost unbreakable mass, safely portable because there is no glass to break nor liquid to spill.

The **units for measurement** of electricity are named after the most celebrated workers in this field. They are based upon the observed analogy of the electric substance to a fluid flowing invisibly as a current from a reservoir which creates pressure according to its height, through conduits which discharge it into various machines for doing work like water lead to a turbine or mill-wheel. The amount of work (*Watt*) depends on the quantity of electricity passing in a second of time (*Ampère*) and also on the pressure driving the current (*Volt*).

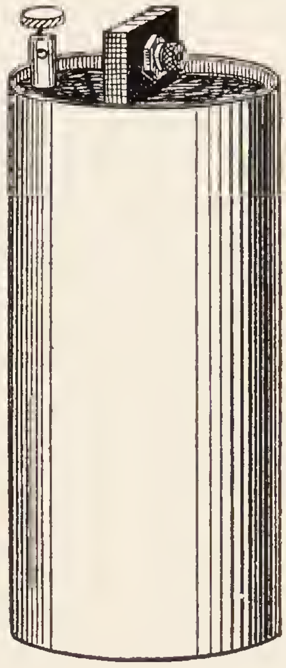


Fig. 14.—Dry battery.

Ampère: the *unit* of current-strength produced by the difference of potential of a volt through the resistance of an ohm. *Ohm's law:* Ampères = volts ÷ ohms, or volts = ampères × ohms. In electrolysis one ampère frees 1.01 gm. of hydrogen in 96,540 seconds.

Milliampère: the thousandth part of an ampère, of which from 1 to 100 or more may be administered to a patient for medical purposes.

Coulomb: the unit of quantity conveyed by the current of an ampère in a second. For the evolution of 1.01 gm. of hydrogen by electrolysis 96.540 coulombs must pass through the electrolyte.

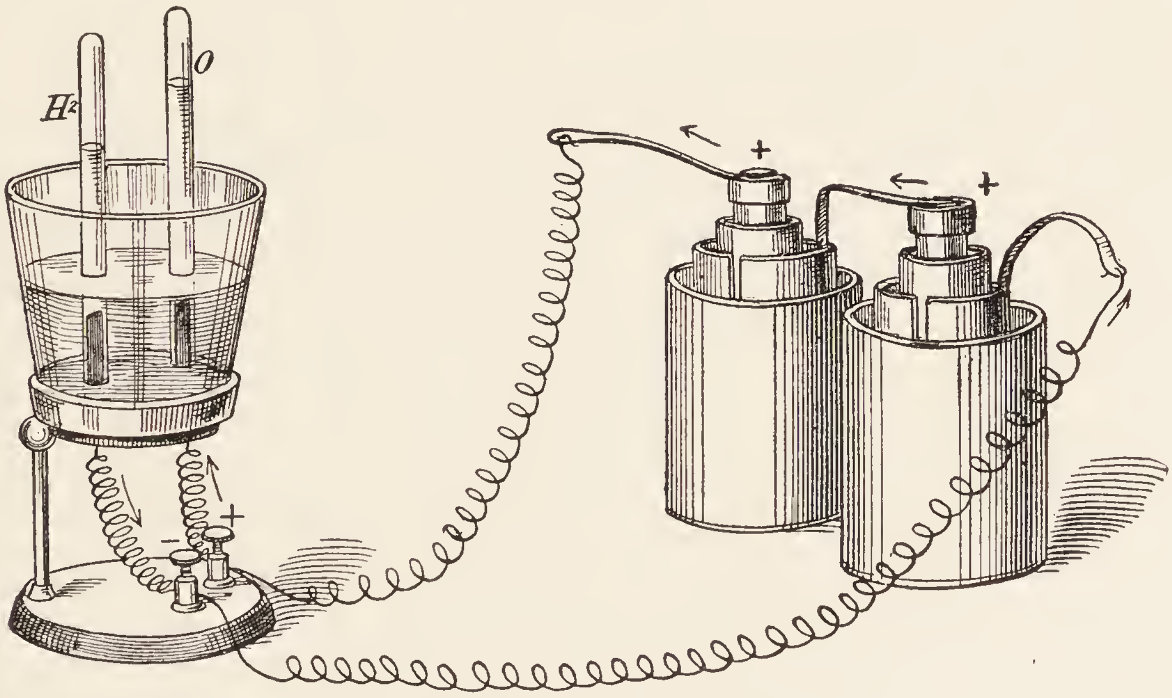


Fig. 15.—Electrolysis of water: Two volumes of hydrogen at the negative pole and one volume of oxygen at the positive pole.

Farad: the unit of electric capacity; the quantity which, with the electromotive force of a volt, would flow through the resistance of an ohm in one second.

Ohm: the unit of resistance offered to a current of electricity by a wire of pure silver or copper one millimeter in diameter and

48.61 meters long at 18.3° C. (65° F.). The resistance of the Atlantic cable is 700 ohms.

Volt: the unit of electromotive force. It equals .9268 of the force of one Daniell cell, or .5 the power of a Grenet cell, or .75 the power of a Leclanché cell.

Watt: the unit of electric power exerted when the current has the strength of one ampère and the electromotive force of one volt. Equal to $\frac{1}{746}$ of a horse power.

It has been stated above that the current flowing through connected polar wires has magnetic properties. The deviation of a magnetic needle caused by it is increased by encircling the needle a number of turns of the insulated conducting wire. In the *milliampère-meter*, or *milam-meter*, such a needle moves over a graduated arc, the degrees indicated corresponding to the current-strength. In medical practice from 1 to 100 or more milliampères are employed, according to the needs of the case.

To lower the current-strength, the number of cells thrown into the circuit is diminished by a switchboard, or the battery remaining the same, resisting material is introduced in the length of the conductor. A *rheostat* is an apparatus for varying and controlling the current-strength by adjusting the resistance. It may be made of coils of iron or German silver wire, or intercalations of carbon or water may be used, all of these being poorer conductors than the copper wire.

Besides the magnetic effects, the current has physical powers familiar in the electric lights, heaters, and motors.

Joule: this unit of work energy equals 0.239 calories heat energy, the power required to raise the potential of one coulomb one volt. To raise one pound one foot high requires 1.326 joules.

Kilo-joule: one thousand joules.

Chemical Effects of the Current.—The passage of electricity through acidulated water is attended by the chemical decomposition of the water into its elements, hydrogen and oxygen. This is *electrolysis*, and acidulated water is called an *electrolyte*. If a solution of copper sulphate ($CuSO_4$) be put into the electrolytic cell and the current sent through it by platinum electrodes, the salt is broken up into its *ions*—copper (Cu) and the group (SO_4). Metallic copper comes to the negative pole, or *cathode*, just as did the hydrogen of the water; hence the metals and hydrogen are known as *cations*. The group (SO_4) engages in a second chemical action upon the water of the solution, decomposing the water and setting free the oxygen, which bubbles off at the positive pole or *anode*, and hence is called the *anion*.

$$SO_4 + \underset{\text{Water.}}{H_2O} = \underset{\text{Acid sulphuric.}}{H_2SO_4} + \underset{\text{Oxygen.}}{O}$$

When a solution of sodium sulphate (Na_2SO_4) is the electrolyte, the first separation is into the cation, sodium (Na) and the anion (SO_4). The metal sodium at once acts on the water present, producing sodium hydroxid and liberating hydrogen, which escapes at the cathode—

$$Na_2 + 2H_2O = 2NaOH + H_2.$$

In this case also there is a secondary decomposition of the water by the SO_4 taking the H_2 and freeing the oxygen (Fig. 15).

All acids, bases, and salts which dissolve and make good conductors are electrolytes and are decomposable. Many salts liquefied by fusion, such as the fused chlorids and hydroxids of various metals, are split by the current. In all such cases the metal, like the hydrogen ion, wanders to the cathode, and the other constituent or ion—the non-metal—goes to the anode. Below is a list of some of the elements arranged in a U-shape so as to show their electric relations. Any element enumerated is found to act as electronegative to those following it, and electropositive to those named before. Speaking generally, those between hydrogen and the negative end are called *electronegative*, and form anions; those toward the positive end are *electropositive*, and form cations.

Negative end.	*Positive end.*
Oxygen.	Potassium.
Sulphur.	Sodium.
Nitrogen.	Lithium.
Fluorin.	Barium.
Chlorin.	Strontium.
Bromin.	Calcium.
Iodin.	Magnesium.
Selenium.	Aluminum.
Phosphorus.	Manganese.
Arsenic.	Zinc.
Chromium.	Iron.
Vanadium.	Nickel.
Molybdenum.	Lead.
Tungsten.	Tin.
Boron.	Bismuth.
Carbon.	Copper.
Antimony.	Silver.
Tellurium.	Mercury.
Tantalum.	Platinum.
Silicon.	Gold.

Hydrogen.

Electrolysis is subject to certain definite laws based upon the principle of chemical equivalence among the elements. In the electrolysis of copper sulphate mentioned above, or of other metallic salts, a given current liberates the metals in weights proportionate to their chemical equivalents.

Hence **Faraday's laws:** (1) "*All the cells in a circuit have in them equivalent amounts of chemical action.*" (2) "*In a given time the chemical action in a cell is directly proportionate to the current-strength.*"

The same current acting separately on a chlorid, a bromid, and an iodid liberates 35 gm. of chlorin, 80 gm. of bromin, and 127 gm. of iodin. These figures are recognized in other relations as the equivalents (p. 63) of these elements.

The gram weights of an element set free in one second by a current-strength of one ampère is called the *electrochemical equivalent.* That of hydrogen being 0.00001038, from law (1) we deduce that to calculate the electrochemical equivalent of any other element, it is only necessary to multiply 0.00001038 by the chemical equivalent of that element. The chemical equivalent of an element is obtained by dividing the valency into the atomic weight (p. 114).

Example: The chemical equivalent of copper being 63.2, how many grams will be deposited by 1 ampère in 1 second? Answer: $63.2 \times 0.00001038 = 0.00656$ gm.

From law (2) we deduce that the mass of copper liberated is equal to the product obtained by multiplying the current-strength by the number of seconds, and then by the chemical equivalent.

The Ion Theory.—The best explanation of the facts of electrolysis is afforded by the theory of *electrolytic dissociation.* It assumes that aqueous solutions of salts, strong acids, and bases contain some entire molecules of the compounds and some that are separated into *ions*, having charges of electricity. The ions with their opposite + and − electricities are attracted to the opposite − and + poles, and thus the molecule is split into its constituents, other entire molecules become *ionized* to take their place, and these in turn are decomposed. The *ion theory* has many phenomena of heat and chemical action to support it (see pp. 128–132).

THE INDUCTION COIL

When the galvanic current passes through a wire (primary), it *induces* another current in a wire (secondary) near to it. If the coarse *primary* wire be insulated and coiled about a core of iron, *A*, Fig. 16, and a much longer and finer wire is wound outside, the ends of this *secondary* wire give remarkable displays of electro-

motive force far in excess of those obtainable from batteries or electric lighting circuits. Nothing is seen so long as the primary current is flowing, but when it is broken a vivid spark passes, owing to the current *induced* in the secondary coil by the interruption of that in the primary. To secure a stream of sparks a rapid opening

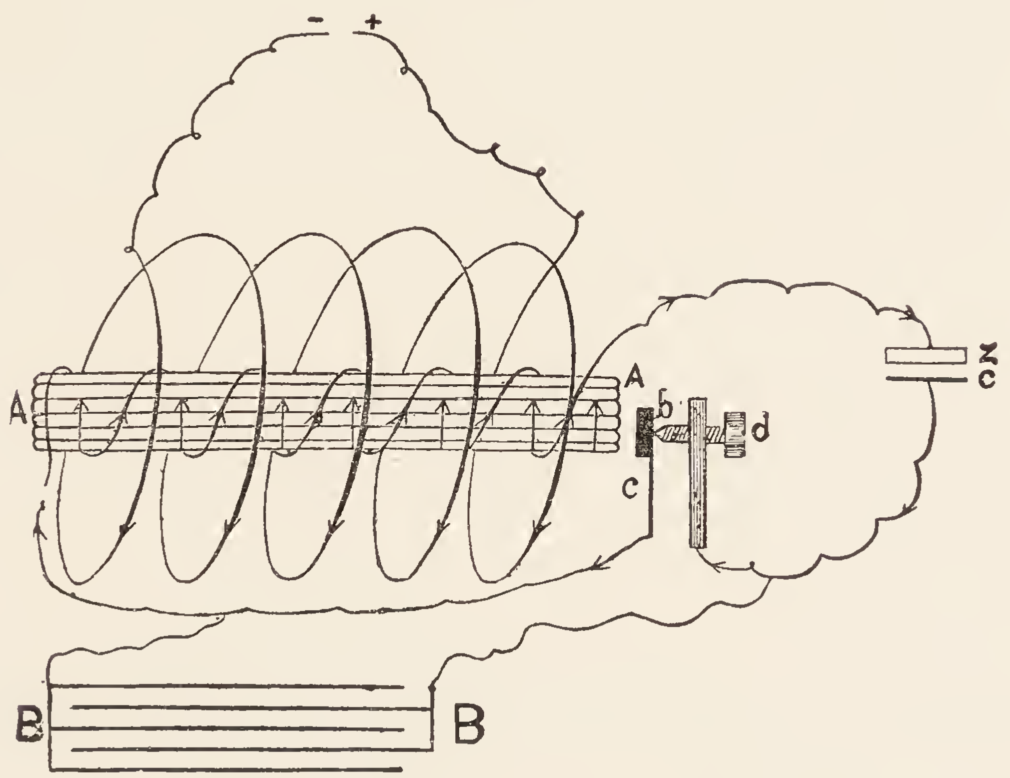


Fig. 16.—Induction coil. A, Core of iron rods; B, condenser, to get rid of the *extra* current which runs back on the *induced* current; C, spring of interrupter; b, iron armature; d, set screw carrying platinum point; z c, battery, — and + are the secondary poles.

and closing is produced in the primary current by an automatic interrupter *C* which is actuated by the electromagnetism of the central iron core. The sparks, coming close together, give intense effects, apparently continuous, which are called the faradic, induced, or secondary current.

CATHODE AND RÖNTGEN RAYS

Under ordinary conditions an insulated body charged by electricity retains its charge owing to the fact that the air at normal pressure offers high resistance to leakage. The electricity of high potential produced by an influenced electrical machine or an induction coil overcomes this resistance and a sudden spark discharges the electrified body. By lowering the air pressure with a pump the spark changes in appearance to a luminous cloud with brilliant bands.

If the metallic electrodes are fused into a glass bulb which is exhausted of air (Crookes' tube) and a powerful induced current passes, giving a spark of 6 inches, the negative electrode (cathode) is seen as a disc surrounded by a pale glow beyond which is a dark

space which extends to the other side of the bulb. The glass directly opposite the cathode disc glows brilliantly with a phosphorescent light, which ordinarily is green from the soda in the glass. Negative electricity streams from the cathode disc in straight lines until it impinges upon the glass wall or the disc of the anode as a target. These "*cathode rays*" are considered to be a flight of negatively electrified corpuscles (*electrons*), which are the same no matter what the material of the disc from which they are driven. They move with a speed nearly equal to that of light, and have a mass a thousand times less than that of a hydrogen atom. While they do not penetrate the glass wall of the bulb, they can pass through a window in it made of aluminium foil, which is of lower density, and when outside are known as *Lenard rays*.

Beside these rays the glass of the bulb transmits a very different set of invisible rays which are produced by the impact of the

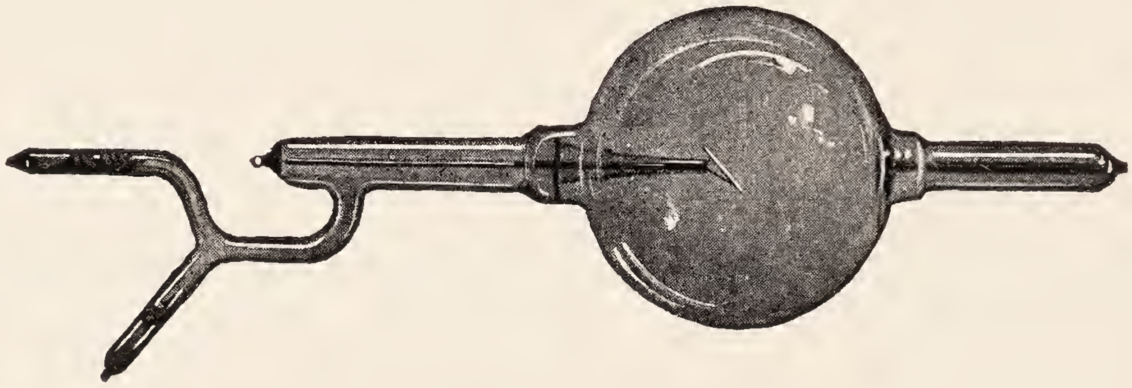


Fig. 17.—Thomson's vacuum regulator tube.

electrons upon the glass wall or the target of the anode. They not only pass through the glass and light up the dark screen of a *fluoroscope* covered with barium or calcium tungstate, affect photograph plates, and act physiologically on animal tissues and organs, but do these things after penetrating enclosures made of opaque substances. They are called "*x*-rays," because their nature was at first unknown, and *Röntgen rays*, after their discoverer. They are supposed to be due to irregular pulsations in the ether, (not a train of waves) caused by the bombardment of the target with the electrons. The rays are absorbed by different materials of a given thickness, roughly in proportion to their density. As dense bodies like bone or metal absorb more than flesh and leather, the rays penetrating a part of the animal body or a leather purse and afterward striking a photograph plate or a fluoroscope, make a shadow picture (skiagraph) of the bones in the flesh or the coins in a purse.

Cathode rays are also emitted from certain substances without the electric discharge, but after exposure to light especially to the ultra-violet. The radio-active metals, uranium, thorium, actinium,

polonium, and radium give off both cathode and Röntgen rays incessantly, without the stimulus of light or electricity (p. 247).

Another important property of the Röntgen ray is that of converting non-conducting air or other gases into conductors of electricity. The charge of an electroscope disappears when it is brought near any radio-active body, the rapidity of this silent discharge being proportional to the radio-activity. The air is supposed to be ionized by the contact of the radiating electrons, and the ions carry off the electricity.

LIGHT

SPECTROSCOPY

When a round beam of white light, *S* (Fig. 18), passes through a prism, *P*, it does not pursue a straight course, as a pencil of light, to form a white circle at *K*, but is bent or *refracted* at an angle toward the base of the prism. On emerging from the prism it is found to be decomposed into different colored lights which diverge to form, on the screen *H*, a brilliant band called the *spectrum*. This dispersion of the component colors is due to the

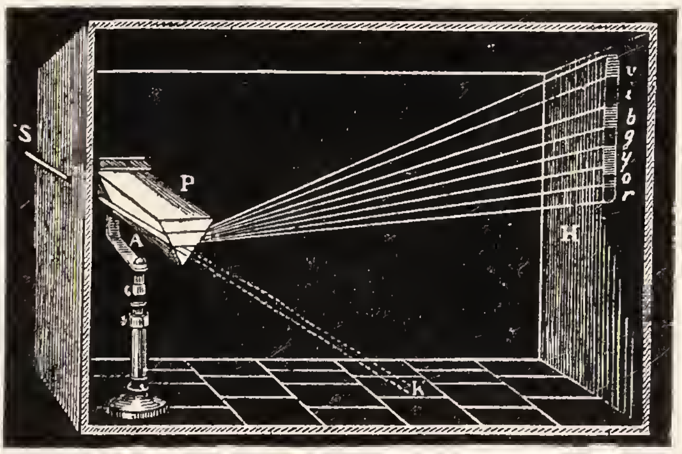


FIG. 18.—Dispersion by a prism.

fact that the several colored lights have unequal wave-lengths. The dense medium of the prism retards the short waves more than the long ones, and hence the short waves of violet at one end are refracted more than the longer ones of red at the other end. In the *continuous spectrum* from the light of candles, lamps, or incandescent solids, six principal groups of colors are designated: *violet*, *blue*, *green*, *yellow*, *orange*, and *red*. If the artificial light have color in it, the spectrum will show that color predominating and the others less bright. (Pl. 4, Fig. 1, *a*.)

When the spectrum is obtained from sunlight passing through

a slit, it appears as a band of bright colors crossed by a number of fine black lines, called *Fraunhofer's lines* (Fig. 19). These are always present in the same relative position. They are considered as shadows caused by the absorption of certain rays in their passage through media. Dark lines or bands crossing the otherwise continuous spectra are obtained by transmission of the pencil of light through colored solids, liquids, or gases. Such spectra are called *absorption spectra*. In Pl. 4, Fig. 1, b, c, d, are shown the dark-banded spectra of blood.

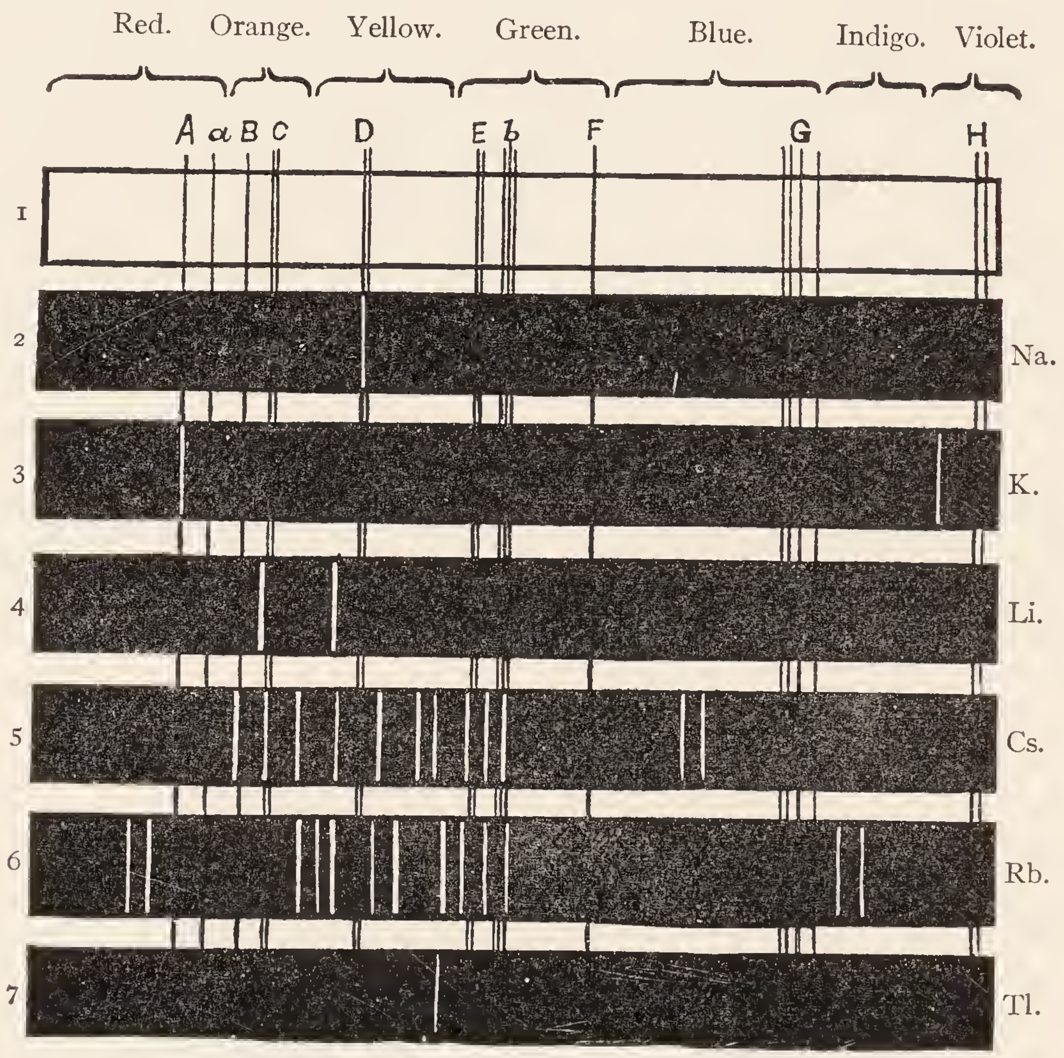


FIG. 19.—Fraunhofer's lines: 1. Solar spectrum (the colors are indicated above); 2–7, bright-line spectra of incandescent gases.

The light emitted by a glowing gas forms a spectrum of disconnected *bright lines* and not of continuous colors, as indicated in the table of spectra of different metals when heated to form incandescent vapors. In Fig. 19 the position of different lines can be determined by reference to the scale at the top, and also by the Fraunhofer's lines. As the spectra of different substances always give different combinations of lines and bands, an important means of identification is afforded by *spectrum analysis*.

The **spectroscope** is an instrument for studying the spectra. It consists of a slit at *v* (Fig. 20), for which there is an adjustable shutter to regulate the beam of light emitted by the incandescent

metal or that transmitted through blood or other colored media. In the telescope *B* there is a lens for collecting the light of the slit in parallel rays and throwing it upon the prism *P*. The telescope *A* serves for the observer to catch the dispersed light after emerging from the prism, and telescope *C* gives the image a standard scale in millimeters, illuminated by the candle *F* and reflected by the face of the prism, so that the observer sees it in front of the spectrum. By this micrometer scale the relative distances of the bands and lines can be noted.

The **direct-vision spectroscope** is a single brass tube having an adjustable slit, a lens focussing the parallel rays upon a series of prisms, two of flint and three of crown glass, arranged in a direct line between the light and the eye. The combination of different prisms decomposes the light without deflecting it from the straight path.

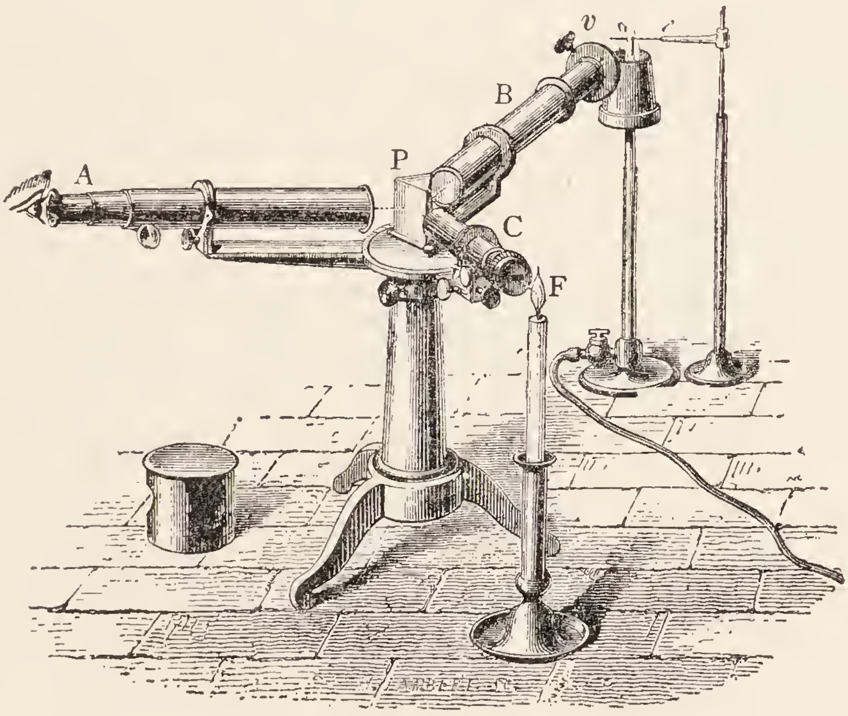


Fig. 20.—Spectroscope.

The spectra in Fig. 19 were exhibited by salts of the metals indicated in symbols when heated on the tip of a platinum needle in a Bunsen flame. The spectrum at the top shows some of the most important of the Fraunhofer dark lines, marked with the letters by which they are usually designated. The spectrum of sodium (Na) has a brilliant yellow line (*D*); potassium (K) has two characteristic lines, one red (*A*), the other violet; lithium (Li), a brilliant red and a fainter orange line. The important lines of strontium (Sr) are in the yellow, red, and blue; barium (Ba), in the green; rubidium (Rb), in the violet and dark red; cesium (Cs), in the blue; and thallium (Tl), in the green.

Beyond the visible limits of the solar spectrum at both ends there are *invisible rays* recognized by their heating (*calorific*) and

their chemical (*actinic*) effects. Not more than one-fourth of the rays of the solar spectrum are visible. At one end the *calorific rays* have longer wave-lengths than the visible red, and hence are called *infrared rays.* At the other end *actinic rays* are more refrangible and have shorter wave-lengths than the luminous violet, and hence are called *ultraviolet rays.* When a solution of quinin sulphate is placed in this dark ultraviolet region, pale-blue rays are seen. Substances which, like quinin and kerosene, have the property of being colorless by transmitted light and of lighting up when observed in reflected light, are said to be *fluorescent.* They lessen the speed of the invisible ultraviolet rays and thus lower their refrangibility, bringing them within the limits perceptible to the eye and reflecting them.

The Ethereal Waves.—The universe is supposed to be pervaded by an elastic medium known as the *ether*, which can vibrate from side to side. The rate of vibrations, according as they are fast or slow, causes a variety of effects. While all of them travel by impulses from their sources at the same speed as light (300,000 kilometers or 186,000 miles a second), their oscillations from side to side may be slower than 2 or 3 to the minute and faster than one million times a minute. The very slow waves are the electric Hertzian waves used in wireless telegraphy; much faster are the waves of radiant dull heat; still faster, red light; then yellow, and on through the colors of the spectrum to violet; at a higher rate are the ultraviolet rays. The x-rays of Röntgen issuing from a Crookes' tube are probably a series of short pulses in the ether sent out at irregular intervals. Being irregular and unlike a train of waves, they are not lost in the regular vibrations of surrounding bodies, but are transmitted with little change.

POLARIMETRY

Iceland spar and some other crystals possess the peculiar property of splitting a transmitted ray of light into two parts. An object viewed through such crystals shows two images, one being made by the *ordinary* rays of light corresponding to single refraction, and the other by the *extra-ordinary*, which differs from the commonly refracted light. If these extraordinary rays are sent through a second similar crystal, and the second crystal be rotated, two of the rays disappear and the field of view becomes dark; further rotation causes return of brightness.

The effect of the first crystal has been to alter the light so that the second crystal, at right angles, does not transmit the modified ray. The light is said to be *polarized*—that is, made to vibrate in one plane. Light commonly vibrates in all planes,

though for convenience it may be regarded as in two planes at right angles. The eye detects no difference between common and polarized light, hence to determine the presence of this property a second crystal must be used, called the *analyzer*. In Fig. 21 the set of vertical rods (A) represents the first crystal or *polarizer*, stopping the rays in a horizontal plane, but allowing the vertical to pass. B is the *analyzer*, placed at right angles, and causing darkness by stopping the rays vibrating in the vertical plane. If B be rotated sufficiently, the polarized ray passes readily and the light reappears.

Having set the polarizer and analyzer at the angle to stop both planes, it is possible to turn the ray of light to the transmitting plane by putting between them certain substances which rotate the rays to the right or left. Among the substances having this rotating property are quartz, the sugars, proteins, and biliary acids; they are classed as *optically active*. Those substances that cause opacity or a shadow when the analyzer is rotated to the right (expressed by the sign +) are said to be *dextrogyrous* (such

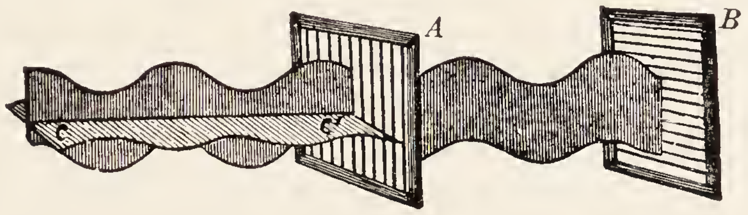


Fig. 21.—Action of polarizer and analyzer.

as dextrose), while those so acting by the opposite movement (expressed by the sign −) are called *levogyrous* (as levulose). Having determined the direction and the number of degrees of rotation of the plane of polarized light caused by a solution, its composition and concentration may be ascertained. The degree of rotation corresponds to the amount of the optically active substance in solution; that is to say, the twist given to the ray depends on the number of molecules which it passes on its way. In the polariscope the polarizing and analyzing crystals used are specially cut rhombs of Iceland spar, called *Nicol's prisms*. These deflect the ordinary ray from the straight path and extinguish it, but permit the extraordinary ray to pass through.

Laurent's half-shadow polarimeter is the instrument seen in section in Fig. 22. At A is a yellow flame, which is best obtained by heating a sodium salt in a Bunsen burner; but a gas flame may be used and the monochromatic yellow color imparted as the light passes through the plate of potassium bichromate at B. It then passes through the Nicol's prism (P), the rays in the horizontal plane emerging as polarized light; those in the per-

pendicular plane are deflected and stopped by a diaphragm. At *D* the light is modified by a diaphragm, one-half of which is covered by a thin plate of quartz, cut so as to have but little rotating power. The circle below *D* shows the diaphragm divided in perpendicular halves by the quartz plate. A tube of brass, 1 decimeter long, closed at both ends with disks of glass, is filled with the solution to be tested and inserted at *T* in the path of the polarized ray.

The eyepiece (*O*) contains a lens and the analyzing prism (*N*), the whole tube rotating on its long axis as the vernier arm is moved around a circle graduated in degrees. When the tube (*T*)

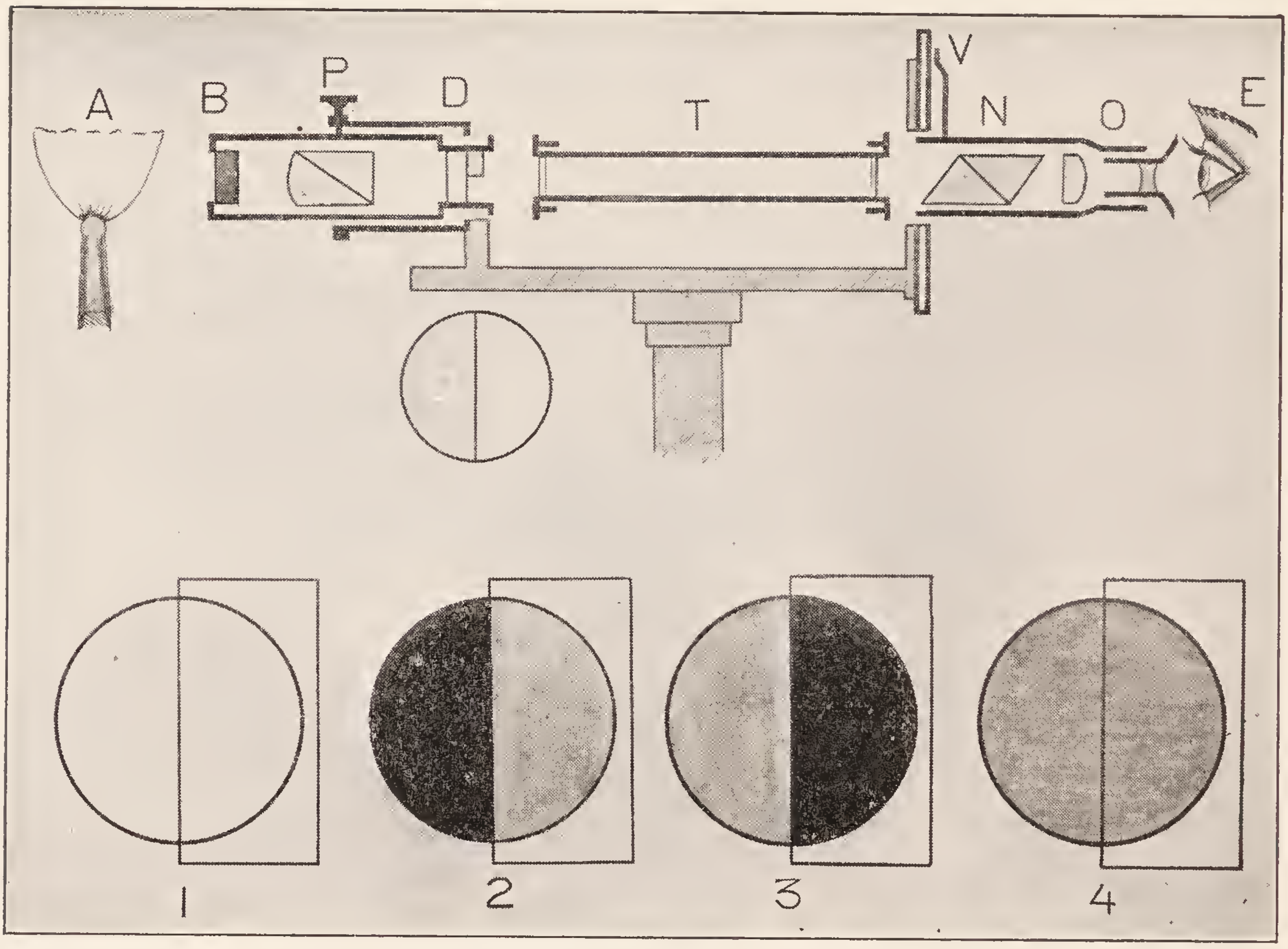


FIG. 22.—Laurent's half-shadow polarimeter.

contains water and the vernier is at 0°, the eyepiece being focused on the vertical line of the diaphragm, the two sides should be equally illuminated, as in the circle 1. If one side be darker, then the polarizer must be rotated by the screw at *P* until both sides are alike. When a solution of sugar or albumin, or other optically active substance, is introduced into the tube only one side of the diaphragm is unshaded, as in circles 2 albumin and 3 sugar. By moving the vernier around the circle, to the left for 2 and to the right for 3, both sides of the diaphragm become equally illuminated, as in circle 4, and the reading of the instrument gives at once the angle of rotation of the solution in the tube (*T*).

The expression *specific rotating power* or *specific rotation* of a

substance means the extent of rotation (expressed in degrees) caused by 1 gm. of that substance dissolved in 1 c.c. of liquid, examined in a tube 1 decimeter long.

If a be the observed angle, p the number of grams of substance in 1 c.c., l the length of the tube in decimeters, and the *specific rotation* for the yellow light (D) of the spectrum be designated by $(a)_D$, then the formula would be $(a)_D = \pm\frac{a}{pl}$. The specific rotation of glucose is stated as $(a)_D = +52.5°$; that is, a rotation of the ray to the right 52.5° is caused by 100 gm. of the substance in 100 c.c. of water. Therefore, with a one-decimeter tube $1° = \frac{100}{52.5}$ gm. in 100 c.c. Example: A specimen of diabetic urine at 0° showed the disc half-shaded, as at 3, Fig. 22, and using a one-decimeter tube (T, Fig. 22) required 2° of dextrorotation to get equal illumination, as in circle 4, Fig. 22, then $\frac{100 \times 2}{52.5} = \frac{200}{52.5} = 3.8$ per cent. glucose.

The **polarimetry of urine** requires that the specimen should first be made free of albumin, which rotates as far to the left (circle 2, Fig. 22) as glucose does to the right (circle 3, Fig. 22), its formula being $(a)_D = -56°$. If albumin be detected, then the urine must be acidulated, boiled, and filtered before testing with the polarimeter.

In most cases of diabetic urine the concentration of sugar is small, and the longer tube (2 decimeters) is used to contain it. With this tube the reading is divided by 2 before the percentage calculation is made; some medical polariscopes are graduated to read percentage of glucose direct.

An accurate adjustment of the reading may require that the urine be decolorized. This is done simply by adding 1 drop of acetic acid and shaking with a test-tube full of urine a small piece of lead acetate and filtering off the precipitate. Another method is to put ½ c.c. of washed blood-charcoal in a test-tube full of urine, then shake and filter. It must be remembered that a trace of maltose may be present, though rarely, and may increase the angle, as it rotates more than glucose—$(a)_D = +140°$. It does not ferment so readily as glucose. Diabetic urine sometimes contains β-oxybutyric acid, which rotates to the left—$(a)_D = -24.2°$—and hence may reduce the glucose reading or neutralize it altogether. The difference between the dextrorotation before fermentation and that afterward would show the presence and amount of the glucose alone. At room temperature 20° C. (68° F.) the specific rotation of cane-sugar is $(a)_D = +66.5°$; malt sugar $+137.0°$; levulose $-93.0°$, and invert sugar $-20.2°$.

THE CHEMICAL ELEMENTS

Chemistry is that branch of science that deals with the properties and composition of substances, and studies the phenomena attending changes of composition.

When water by variations of temperature becomes ice or steam, it has undergone a *physical change*, due to the play between two physical energies: cohesion and heat. When glass or sealing-wax is rubbed it acquires the property of attracting feathers, pith-balls, and paper, by virtue of a transient physical power, the electric energy. When iron is made red-hot or when it is magnetized, it remains iron still, but when it rusts it loses its magnetic qualities and is transformed into a substance of wholly different properties. The energy which rusts iron, which burns coal, which turns milk sour, which changes wine into vinegar is not physical, but chemical.

The chemical energy or affinity acts between different kinds of matter, causing them to lose their characteristic properties in forming a new substance. While its operations are correlated with those of physical energy, it is peculiar in that it produces *permanent change* in bodies. The change is more profound than that induced by *mechanical mixture.*

If powdered iron and powdered sulphur are mixed by trituration in a mortar, to the naked eye a change in color is visible, the yellow and black making brown; but under the microscope we can distinguish the iron particles as separate from those of sulphur. The particles of iron are still magnetic and can be removed by the touch of a magnet. The sulphur can be dissolved out by treating the mixture with carbon bisulphid. When, however, the original mixture is ignited, the iron and the sulphur unite by chemical affinity, and now the microscope fails to detect the two different substances; the magnet will not separate the iron, nor the carbon bisulphid dissolve the sulphur. Chemical energy is distinguished further by the fact that its action is limited to definite weights of matter, while a mechanical mixture can be made of ingredients in any proportion.

All natural objects, suns, planets, the mineral strata of the earth, its bodies of water, and its aërial envelop, the living things that crowd its surface, the molecules and atoms, are held in place by an energy which manifests itself in the phenomena of gravitation, of cohesion, and of chemical affinity. Gravitation affects all forms of matter at all distances; cohesion acts on molecules at distances immeasurably small; chemical affinity acts upon the minute atoms at insensible distances, causing such transformations

of the bodies acted upon that they can no longer be recognized by ordinary means.

Elements and Compounds.—All forms of matter may be divided into two classes, compounds and elements. Most natural objects are compound—that is, bodies that can be decomposed into simpler kinds of matter. They consist of two or more elements united by chemical affinity. *Elements* are the simplest constituents of a compound into which it is decomposed. While some of them occur free in nature, most of them are obtained by chemical separation of the parts of a compound. The resolution of a compound into its parts is called *analysis*, while the building up of a compound by combining its parts is called *synthesis*. Every element has a constant combining equivalent (p. 114) and has never been known to enter any compound in less proportion than this equivalence. It is also characterized by a definite spectrum (p. 55) as a distinct species of matter.

The diversity of matter in the more than 300,000 forms seen in the universe is due to variations in the kind and the proportion of the elements engaged. Science has found from 80 to 100 simple bodies or elements.[1] Of the elements now identified not more than 40 are of any practical medical importance; the others are rarely encountered. Those deserving attention will be found in the following tables, each accompanied by its symbol, which is either the initial letter of the English or Latin name, or that letter combined with a significant small letter taken from the name. The combining equivalents in *round numbers* are given in the third column. These are stated as atomic weights on p. 117.

The elements are broadly divided into two classes: *non-metals* and *metals*, each having properties generally characteristic. *Non-metals* physically have low specific gravity and are poor conductors of heat and electricity; chemically they form acids. *Metals* have high specific gravity and metallic luster, are good conductors of heat and electricity, and form bases.

Some Non-metals

Name.	Symbol.	Combining equivalents.	Name.	Symbol.	Combining equivalents.
Oxygen	O	16	Fluorin	F	19
Hydrogen	H	1	Chlorin	Cl	35.5
Nitrogen	N	14	Bromin	Br	80
Carbon	C	12	Iodin	I	127
Boron	B	11	Sulphur	S	32
Silicon	Si	28	Phosphorus	P	31

[1] To the 80 permanent elements named on page 117 must be added the 28 ephemeral elements transmuted from uranium (p. 249). There is no escape from the conclusion that the cathode electric rays of a Crookes tube are disembodied charges of negative electricity or *electrons*, in which the subdivision is carried much further than in the ordinary molecule or even atom. The atoms of different chemical elements seem to be different aggregations of the same primordial *electrons*. By losing some of these uranium produces radium and helium arises from further losses.

All of the above, except hydrogen and oxygen, form acids when united with those two elements.

Some Metals

Name.	Symbol.	Combining equivalents.	Name.	Symbol.	Combining equivalents.
Potassium	K (Kalium)	39	Zinc	Zn	65
Sodium	Na (Natrium)	23	Nickel	Ni	58
Lithium	Li	7	Cobalt	Co	59
Barium	Ba	137	Iron	Fe (Ferrum)	56
Strontium	Sr	87.5	Manganese	Mn	55
Calcium	Ca	40	Chromium	Cr	52
Magnesium	Mg	24	Tin	Sn (Stannum)	118
Aluminium	Al	27	Copper	Cu (Cuprum)	63
Arsenic	As	75	Lead	Pb (Plumbum)	207
Antimony	Sb (Stibium)	120	Mercury	Hg (Hydrargyrum)	200
Bismuth	Bi	208	Gold	Au (Aurum)	197
Cadmium	Cd	112	Platinum	Pt	195

Some of the above-named metals, such as arsenic and antimony, might with equal reason be classified along with the non-metals nitrogen and phosphorus, which they closely resemble in their chemical traits. Most of the true metals will form bases by union of their oxids with water.

Chemical compounds are usually considered in two great classes, the *Inorganic* and the *Organic*, though the line of demarcation is one made for convenience and is not drawn by nature. *Inorganic compounds* are of mineral origin, not requiring a living organism to produce them. Examples are water, lime, and common salt. *Organic compounds* are those which, as found in nature, are produced exclusively by the action of organized animal or vegetable life. Examples are fat, albumin, starch, and sugar. As carbon is invariably present in organic substances, organic compounds are sometimes called *carbon compounds*. Beside carbon, they usually contain oxygen and hydrogen, and very often nitrogen. Owing to the marked traits of these four non-metals, they are especially fitted for study as types illustrating the principles of chemical philosophy. Hence they are often termed *Typic Elements*. They are of the greatest importance to the physiologist in his study of nutrition and animal heat. On these accounts in the following pages extended treatment is given to the compounds of these elements.

The body of a living animal is about two-thirds water and one-third solids. The solids exist as more or less complex compounds of elements, which are abundant in the following order of percentage: Oxygen, 66.0; carbon, 17.5; hydrogen, 10.2; nitrogen, 2.4; calcium, 1.6; phosphorus, 0.9; potassium, 0.3; sodium, 0.3; chlorin, 0.3; sulphur, 0.2; magnesium, 0.05; iron, 0.004; and traces of iodin, fluorin, silicon, copper, manganese, and lithium.

Notation.—The symbols H, O, etc., stand not only for the element, but for a chemical unit of the element. When more than one unit is expressed a large numeral is written before, multiplying all the symbols that follow it, as 2H, or a small numeral is placed to the right and below the symbol, as H_2, for 2 units of hydrogen. To express admixture of elements the plus sign is used, thus $H_2 + O$ means that 2 units of hydrogen are mixed with 1 of oxygen. To express union or combination the symbols are put as close together as the type will go; thus $2H_2O$ means two parts of the compound formed when hydrogen, two units, and oxygen, one unit, unite by chemical attraction.

NON-METALS

Classification.—It is assumed that the medical student is a beginner in chemistry, and as yet is unfitted to appreciate the reasons for arranging the elements according to the natural or scientific classification (see page 116). The considerations which make the most logical system desirable will be understood only after the principles of chemical philosophy have been studied. These principles will be elucidated in the course of studying the *Typic Elements*—oxygen, hydrogen, nitrogen, and carbon, and their compounds. These will be first considered in the order best suited for the intellectual needs of the student, though reference will be made to the more systematic grouping given below:

GROUP I. Hydrogen, unique (Monovalent).
GROUP II. Halogens or the *chlorin family*: chlorin, bromin, iodin, and fluorin (Monovalent).
GROUP III. The *oxygen family*: oxygen, sulphur, selenium, and tellurium (Divalent).
GROUP IV. The *nitrogen family*: nitrogen, phosphorus, arsenic, and antimony (Trivalent).
GROUP V. The *argon family*: argon, helium, neon, crypton, xenon.
GROUP VI. The *carbon family*: carbon, silicon, (Quadrivalent).

OXYGEN

Symbol, O. Atomic weight, 16.

History.—The discovery of oxygen was an incident in the study of the composition of the atmosphere. The early Greek philosophers regarded the air as an element, as they did the earth, fire, and water.

Its complex nature was suspected when, early in the seventeenth century, the observation was made that by combustion in a

confined portion of air, the air lost weight, and that the remainder would support neither life nor fire. Priestley showed that by heating mercury in enclosed air for several days at a temperature near its boiling-point, the mercury was changed to a red powder, now called mercuric oxid, while the life-sustaining part of the air disappeared. In 1774 he found that by heating mercuric oxid a gas was liberated which, when mixed with the burnt-out air, would restore to it the properties of supporting respiration and combustion.

This operation is performed in a hard glass reduction tube or retort, and the gas collected over water in a pneumatic trough, the mercury being condensed on the cooler part of the glass tube. The result may be written as follows:

Mercuric oxid yields mercury and oxygen.

Or, by short hand,

$$HgO = Hg + O.$$

Preparation.—Many higher oxids, as manganese dioxid, MnO_2; lead dioxid, PbO_2; and barium dioxid BaO_2, yield a part of their oxygen when heated. Barium dioxid above 400° C. (752° F.) gives off half of its oxygen.

$$\underset{\text{Barium dioxid.}}{BaO_2} = \underset{\text{Barium monoxid.}}{BaO} + O.$$

This lower oxid, BaO, heated at a lower temperature in a current of air, takes up the oxygen it had lost. By alternating these processes oxygen is now manufactured on a commercial scale at a low cost.

The alkaline peroxides are convenient sources. Fused sodium dioxid with a fractional per cent. of copper oxid is sold for this purpose as "Oxone." Put in water it yields half of its oxygen.

$$Na_2O_2 = Na_2O + O.$$

In the laboratory potassium chlorate is the source. When this compound is heated, it parts with its oxygen, leaving potassium chlorid in the retort.

$$\underset{\text{Potassium chlorate.}}{KClO_3} = \underset{\text{Potassium chlorid.}}{KCl} + 3O.$$

It is customary to employ a mixture of coarsely powdered manganese dioxid 1 part and potassium chlorate 2 parts. This causes the $KClO_3$ to yield oxygen at a comparatively low tem-

perature, 200° C. (372° F.). The manganese dioxid is not decomposed, though its presence causes the easy transmission of oxygen from the chlorate.

Precaution.—The materials should be dry and free from organic dirt. Serious explosions have happened from the action of oxygen on the carbon of coal-dust or other impurities in commercial manganese dioxid. To guard against such accidents

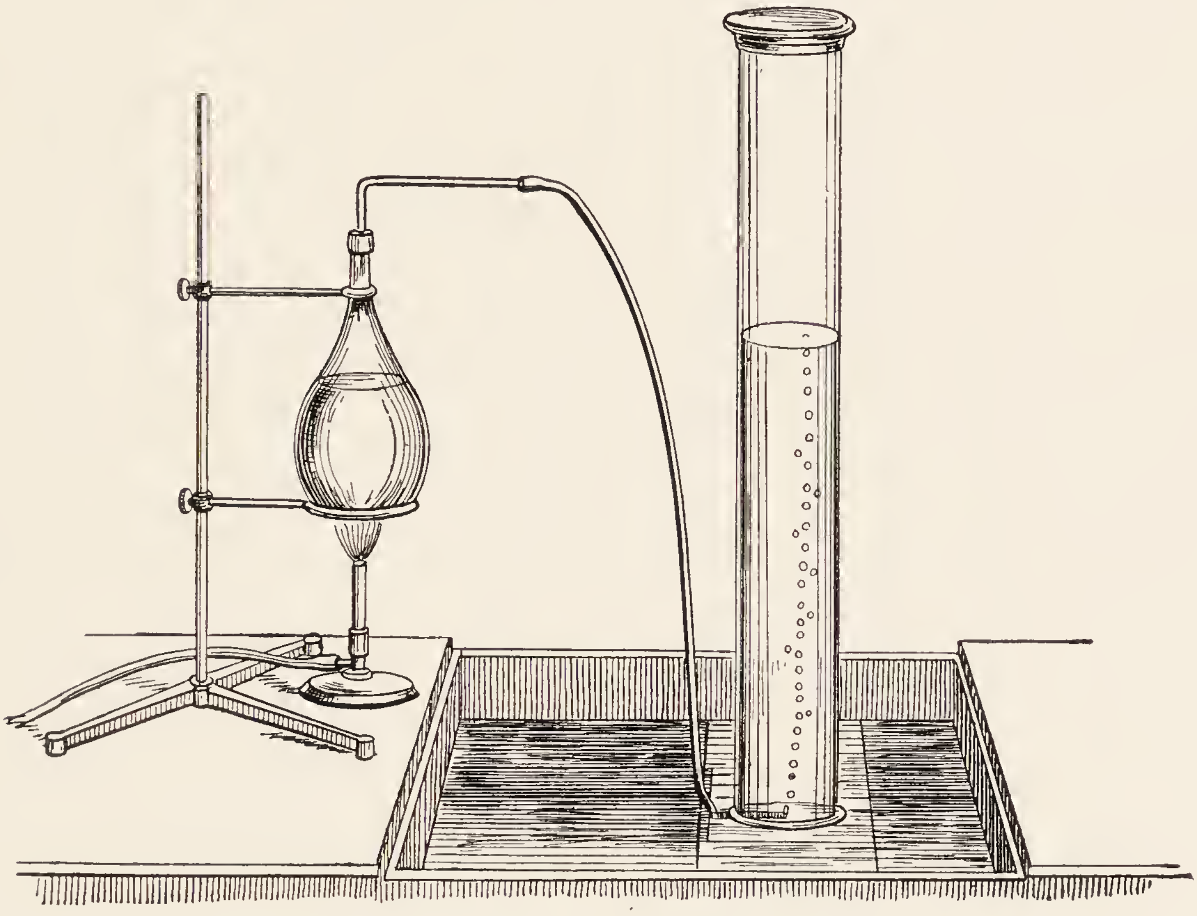


Fig. 23.—Collection of gas disengaged by heat.

a small sample should be tested by heating with some potassium chlorate in an open test-tube.

In preparing oxygen for inhalation it is advisable to free it from all traces of chlorin by passing the gas through potassium hydroxid in a wash bottle before collecting it in the gas bags or gasometer. Before removing the lamp withdraw the delivery tube from the water, if collected in a pneumatic trough, or the regurgitation of the water will cause an explosion. In making a quantity of the gas it is customary to use a copper retort for the potassium chlorate. In practice 250 gm. (8 oz., Troy) of the chlorate yields about 68 L. (18 gal.) of oxygen gas.

Occurrence.—Oxygen is the most abundant element. It is found widely distributed in nature, forming one-fifth part of the volume of the air and eight-ninths, by weight, of all water. As an ingredient in most minerals it makes up nearly one-half of the weight of the earth's crust, and it is present in almost all animal and vegetable compounds.

Physical Properties.—Oxygen is a little heavier than air, its specific gravity being 1.10563 (air = 1). It is an invisible gas, colorless, tasteless, and odorless. It is slightly soluble in water, 0.04 volume dissolving in 1 volume of water at 0° C. (32° F.). In the proportion of about 3 per cent. by volume it is dissolved in natural water at ordinary temperatures, and furnishes to the gills of fishes the amount needed for the aëration of their blood. It becomes a pale blue liquid at −118° C. (−244.4° F.) under a pressure of 50 atmospheres. These are called its *critical values*.

Chemical Properties.—It has affinities of great power and wide range, combining with every element except fluorin and the argon group. As the air is practically one-fifth part oxygen diluted, all its chemical reactions are those of this gas. There is this difference only: the pure oxygen causes far more intense displays of energy. By attaching various combustibles to copper wire, first igniting them in the air and afterward plunging them into jars of pure oxygen, the contrast will show how much the diluent of the air mitigates the violent action of this gas. Sulphur will burn in the air with a pale blue flame of little luminous power; in oxygen, however, its flame is violet colored, emitting great light.

$$\underset{\text{Sulphur.}}{S} + O_2 = \underset{\text{Sulphur dioxid.}}{SO_2}$$

A piece of charcoal with a feeble spark and without flame, when immersed in oxygen, becomes a white, glowing mass and is instantly consumed in flames. A glowing chip of wood is a *reagent* in testing for oxygen and the *reaction* is its bursting into flame.

$$\underset{\text{Carbon.}}{C} + O_2 = \underset{\text{Carbon dioxid.}}{CO_2}$$

If a piece of dry phosphorus the size of a pea be warmed in a deflagrating spoon and then burned in oxygen, its light is of insupportable brilliancy.

$$\underset{\text{Phosphorus.}}{2P} + 5O = \underset{\text{Phosphorus pentoxid.}}{P_2O_5}$$

Fine iron piano wire or watch springs tipped with burning sulphur and set on fire in oxygen will burn with dazzling corruscations.

$$\underset{\text{Iron.}}{3Fe} + 4O = \underset{\text{Iron tetroxid.}}{Fe_3O_4}$$

The non-metals burning in oxygen yield *oxids*, which in the cases of sulphur, carbon, and phosphorus are gases that will dissolve in the

water in the jar, giving to it a sour taste and an acid reaction. Iron forms a solid oxid without acid qualities, which leaves a rusty stain on the jar. Most metals form oxids, which in water change to *bases*.

The presence of free oxygen is revealed by adding to the suspected sample the colorless gas nitrogen dioxid, which unites with more oxygen to form red fumes of the higher oxids. Free oxygen is removed from mixtures of gases by means of its slow union with phosphorus or by making use of the absorption powers of a solution of potassium pyrogallate.

Physiologic Effect.—Oxyhemoglobin of the blood-corpuscles under the air-pump yields about two volumes of oxygen, which is so loosely associated as to be separable without destruction of the compound. This load is readily transferable to oxidizable substances. The muscles and, indeed, protoplasm in general, have the power of absorbing and storing up oxygen to be utilized in the transforming of chemical into other forms of energy. If an animal be enclosed in an atmosphere containing no oxygen it shortly dies. It is the only pure gas that will sustain respiration. At ordinary pressures no detriment follows its inhalation. When disease interferes with normal oxygenation of the blood benefit is obtained by enriching the air respired with about 60 per cent. of this gas. The livid appearance disappears under its judicious employment.

Uses.—The gas is made portable by condensing 40 gallons in a small cylinder. By a rubber tube it is transmitted to a funnel held near the face of the patient. It is used in this way in the treatment of the later stages of pneumonia and consumption and in resuscitation from coal-gas poisoning.

Law of Chemical Combination.—When Priestley, on the discovery of oxygen, resorted to the balance, he was able to prove that mercuric oxid contains an unvarying amount of oxygen joined to an unvarying proportion of mercury. When the two elements in these fixed proportions were caused to combine they produced the compound. Any excess of ether would not enter into the union.

Potassium chlorate, when analyzed and its constituents weighed, is found to be composed of 39 parts of potassium, 35.5 parts of chlorin, and 48 parts of oxygen. All specimens of potassium chlorate have exactly this composition.

When the composition of a salt is once ascertained, the knowledge thus obtained applies to all samples of that salt. Common salt is, always and everywhere, sodium 23 parts and chlorin 35.5 parts.

When it is desired to make note of a chemical operation in shorthand, symbols are used to express both the nature of the elements and the relative weights engaged. Thus the equation,

$$KClO_3 = KCl + 3O,$$

written out in full, would read: potassium chlorate 122.5 (potassium 39 parts, chlorin 35.5, and oxygen 48) yields potassium chlorid 74.5 (potassium 39, chlorin 35.5) and oxygen 48 parts.

If these figures on each side of the equation are added, they will be found to be equal, though the = mark is not used in an algebraic sense; it means *gives* or *yields*.

Reactions.—We have learned that mercury, heated in air, takes up oxygen, forming mercuric oxid, $Hg + O = HgO$. This is an illustration of the first kind of reaction, called *combination*. The second kind is called *decomposition*, as in the case of $KClO_3$, given above, which reverses combination. The third kind is *double* decomposition, when two or more compounds break up and form two or more others, thus:

$$KCl + AgNO_3 = AgCl + KNO_3.$$

This is read, potassium chlorid added to silver nitrate gives silver chlorid and potassium nitrate.

When the composition of many compounds is studied it is found that the most satisfactory unit for expressing the numeric ratios of the combining weights is that of hydrogen, the lightest element. The different symbols stand, then, not only for the name, but also for certain relative weights or proportions (H being 1) in which the elements unite, or those in which they displace one another in compounds.

H stands for 1 part of hydrogen, O for 16 parts of oxygen, O_3 for 3 times 16 or 48 parts of oxygen, K for 39 parts of potassium, S for 32 parts of sulphur, C for 12 parts of carbon.

A convenient statement of the facts just referred to is called the *law of definite or constant proportions* or *combination:*

"A definite chemical compound always contains the same elements united in the same proportions."

This law, discovered by Lavoisier in the eighteenth century, by numerous experiments became more and more assured, and the great generalization gradually took shape—that *matter is indestructible.* So far as our observation goes, it is not created, nor is it destroyed. It may change its form a thousand times, but does not change its ultimate nature, neither gaining nor losing.

When a piece of charcoal is burned in oxygen it disappears from view, but if the product contained in the vessel be weighed it will be found to equal exactly the weight of the original materials. The carbon has been taken into an invisible gaseous compound, carbon dioxid. From this state it can be recovered in the original amount as fine black dust by burning sodium in the gas. The sodium liberates the carbon, taking the oxygen away from it.

When $KClO_3$ has yielded its oxygen there is left in the retort KCl, potassium chlorid, composed of potassium 39 parts and chlorin 35.5 parts. There is a familiar salt used in medicine, potassium iodid, which is composed of potassium 39 parts and iodin 127. Now when chlorin and iodin unite to form iodin chlorid, they do so in the same relative weight, 35.5 to 127. Dependent upon facts of the same character is the corollary to the first law, which is called the *law of equivalent proportions:*

"The proportions in which any two elements unite with a third are the same in which they unite with each other."

Hence it is said that chlorin 35.5, iodin 127, oxygen 16, sodium 23, potassium 39, are equivalent to each other, taking hydrogen as unity. Every element has an assigned equivalent weight, which rules the proportions of its combinations with other elements.

Chemical Arithmetic.—The constancy of the proportions in chemical compounds definitely distinguishes them from mechanical mixtures. When active chemicals are mixed in any other than the exact proportion, the excess is inert. Chemistry is based so surely upon numeric laws that calculations can be made for chemical operations as for those of other exact sciences.

Suppose the problem to be: how much of the gas would be obtained by heating a weight of, say 250 gm. (8 oz., Troy), of potassium chlorate. The equation, already given, is as follows:

$$KClO_3 \quad = \quad KCl \quad + \quad 3O.$$

From the numeric values given for this equation (p. 69) we calculate that 122.5 parts of $KClO_3$ will, when heated, give up 48 parts of oxygen. By a sum in rule-of-three (ratio and proportion) we easily find how many would be given by 250 gm. of $KClO_3$:

$$122.5 : 250 :: 48 : x$$
$$x = 97.95 \text{ gm. of oxygen.}$$

If it be desired to know the number of liters represented by the weight of 97.95 gm. an additional calculation is required. Experiments show that 22.4 L. of any normal gas weigh a number of grams equal to twice the combining weight. Then one-half, or 11.2, would equal the combining weight, which, with oxygen, is 16. Therefore,

$$16 : 97.95 :: 11.2 : x$$
$$x = 68.56 \text{ L. of oxygen evolved from 250 gm. of potassium chlorate.}$$

Relations of Other Forces to Chemical Energy.—Melting solids by heat, or at higher temperatures vaporizing them, favors chemical change. Furthermore, all changes of decomposition or of combination are set in action by the physical agencies, radiant energy, heat, light, electricity, magnetism, and mechanical force. These are convertible into one another and are but forms of the one energy in the universe.

When potassium chlorate is heated to a high degree its particles are freed from their cohesion and chemical affinity under new conditions of temperature forms a different compound, setting the oxygen free.

At ordinary temperatures carbon remains in oxygen for a long time without visible change, though if coal be finely divided and packed so as to confine the heat that is produced by its gradual oxidation, it ignites spontaneously. Whenever carbon is heated to ignition there is immediate union with the oxygen. Moreover, the union is itself attended by the evolution of still more heat. In the oxygen experiments the degree of heat is so great that a brilliant light is emitted. Burning in air is the same as burning in oxygen, though the visible heat is less because the diluent nitrogen in air takes up the heat without helping on the process, while in pure oxygen the chemical energy of that active gas is increased by its being heated. The term *combustion* is applied to this evolution of heat and light by chemical action. Combustion is due to the conversion of *internal* or chemical energy into heat energy. The substances that burn are called *combustible*. The process converts them into *incombustible* products, such as carbon dioxid and sulphur dioxid. All chemical actions are attended by changes of temperature, but in writing equations it is customary to omit mention of the energy of heat consumed or evolved.

The amount of heat evolved or absorbed in the chemical change of a substance is definite and is always the same from given weights of the reagents. If rapid union be induced, as in combustion, then a higher temperature is noted, but no more heat in quantity is given off than when union is gradual. The number of heat units or *calories* (p. 34) obtained is the same whether combustible bodies are oxidized by degrees or whether the same substances are burnt up. When coal is burned in a grate we have an example of heat production by quick oxidation. When carbon compounds are consumed in our bodies by their union with the oxygen of the blood obtained from respired air, we have an instance of heat production by slow oxidation. A given weight of the combustible will yield the same number of heat units in both cases. One gram of a carbohydrate, such as starch, burned with oxygen in a calorimeter, liberates 4100 calories. In the animal body the same weight of starch is oxidized to the same products (carbon dioxid and water), liberating the same number of calories. Combustion

means that the heat is given off in a short period, evincing great intensity. The process has high velocity. Oxidation in the animal body is distributed through greater periods and regulated so that the escape of heat is compatible with life; indeed, is necessary to it. It is dissipated as fast as it is produced. The velocity is so low that the heat never reaches sufficient intensity to ignite the elements engaged.

To use a homely illustration: if a bucket slowly leaks, a gallon of water can be poured into it at the same rate (slow oxidation) and no water accumulates, but if poured quickly (combustion) the water level rises, stands high in the bucket, and may even overflow. Two-thirds of the amount of heat generated in the body is converted to other forms of energy and escapes by radiation, the remaining one-third finds outlets in the hot urine and feces, which contain much more heat than the cool water drunk; in the latent heat of vaporizing the water of perspiration and respiration; and in warming the air inhaled, which has high specific heat (p. 34).

Thermochemistry.—Elements and compounds must be regarded as stores of *internal* or *chemical energy*. The liberation of part of this as *free* or *available* energy, in the measurable form of heat, is an incident of most chemical changes. Such actions are called *exothermic*, giving off heat, and are indicated by the plus sign in writing their *thermal* equations. Thus the formation of water: $H_2+O=H_2O+67,883$ cal. To bring about certain other chemical changes, energy must be supplied from without. These actions are called *endothermic*, absorbing heat, and are indicated by the minus sign in the thermal equation. Thus the decomposition of mercuric oxid: $HgO=Hg+O-30,660$ cal.

Endothermic compounds are usually unstable, and some are explosive in their readiness to give back the energy absorbed in their formation (p. 97). The heat consumed in slowly oxidizing mercury to form mercuric oxid is the same in amount as that required to decompose it into its elements. To form HgO it takes 30,660 calories, and to separate its elements Hg and O the same number of heat units must be used. The heat equations for formation and decomposition would differ only by being opposite in signs.

Work-energy of Oxidation.—Heat is a source of mechanical motion, as in the steam engine, and, on the other hand, the arrest of motion causes heat. They are reciprocally convertible in definite amounts, a certain amount of work-energy producing a corresponding amount of heat-energy and *vice versa*. This numeric relationship is expressed thus: one *calorie* equals 0.426 kilogram-meters, which is to say, that the amount of heat required to warm one gram of water one degree Centigrade of temperature will, when converted to work-energy, lift 1 kilogram weight through 0.426 meters.

In order to have but one unit for all the different forms of energy, that of Joule has been chosen. Thus 1 calorie (cal.) equals 4.18 joules (j.), or, reversing the statement, 1 joule = 0.239 cal.

Large amounts of energy are expressed by kilojoules (kj.) or 1000 joules. By experiment it is found that the heat of combustion of a combining weight of carbon equals that which produces 406 kj. of work-energy. The equation $C+O_2=CO_2+406$ kj. reads thus: the sum of the internal energy of 12 gm. of carbon and 32 gm. of oxygen equals the energy of 44 gm. of carbon dioxid plus 406 kj. This 406 kj. may be utilized in engines suited for converting heat to motion, or in animals for maintaining the work-energy and animal heat. The energy of CO_2, an incombustible product, is less than that of the combustible C and O by 406 kj. Hence to restore CO_2 to the original state of free C and free O this energy must be supplied. In nature the source of this energy is the sun, which, acting upon the leaves of plants as its instruments, breaks up the CO_2 of the air, storing C in the plant and giving O back to the air (p. 104).

OZONE OR ALLOTROPIC OXYGEN

Symbol, O_3. Molecular weight, 48.

When the sparks of an electric machine are passed through dry air or oxygen a peculiar odor is developed. This odor has been observed after thunder-storms or when flint and steel are struck. The odoriferous substance is named ozone (Greek, *ozein*, to smell).

Occurrence.—Owing to its odor, ozone can be recognized in the air when present in the proportion of only one part to a hundred thousand. Delicate tests detect it in sea air, at the seashore, where water evaporates from sand and where the waves are broken into spray; in the country, and especially in the air of pine forests. On the windward side of cities it can be found, but all trace disappears on the leeward side. The organic impurities emanating from cities destroy the ozone.

Preparation.—Ozone can be produced by slowly oxidizing phosphorus in moist air. A stick of phosphorus, freshly scraped, is put in a wide-mouthed bottle of air or oxygen and half covered with water. The bottle is closed for an hour or two, when, at the end of that time, the ozone is present.

Another method is by adding 2 parts of potassium permanganate to 3 parts of sulphuric acid.

Siemen's induction tube generates ozone by discharging electricity silently through an atmosphere of dry oxygen. A tube of glass covered with tinfoil, like the outer coat of a Leyden jar, encloses the space to be filled with oxygen. In the axis of this tube is

another, smaller and lined inside with tinfoil like the inner coat of a Leyden jar. The dry oxygen slowly traverses the space between the tubes, while the electric discharge from either a friction machine or an induction coil passes invisibly from the tinfoil on one tube, through the glass and oxygen, to the tinfoil on the other tube. In its transit a portion of the odorless oxygen acquires the odor of ozone and will oxidize substances that resist the pure oxygen.

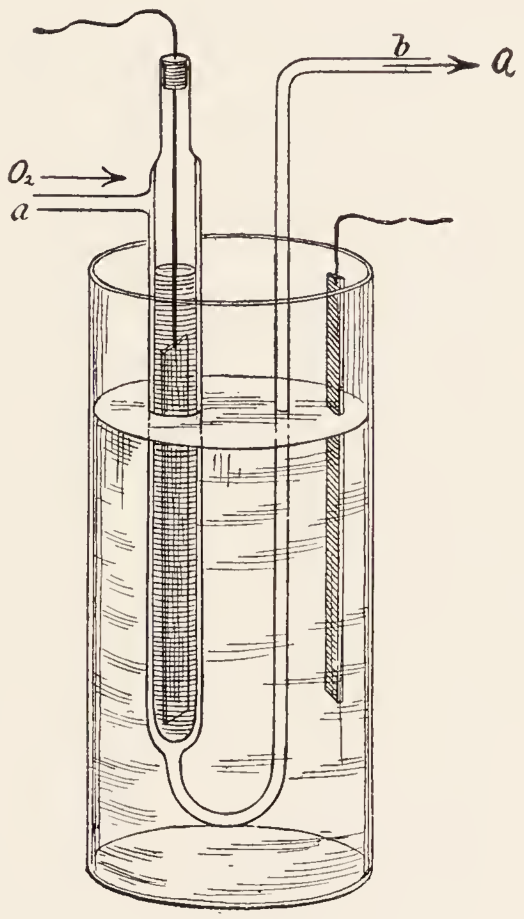


FIG. 24.—Ozone generator.

Instead of tinfoil as a condenser, sulphuric acid is used in the apparatus shown in Fig. 24. A tall glass cylinder containing sulphuric acid has immersed in it a bent tube having one limb larger than the other. The wider limb has an inner tube containing sulphuric acid. Electrodes of platinum dip into the sulphuric acid, inside and outside. While an induction coil discharges between the electrodes, dry oxygen (O_2) passes in at *a* and comes out ozonized (O_3) at *b*.

If ozone be passed into a solution of potassium iodid, the iodin is liberated and potassium hydroxid formed:

$$\underset{\text{Potassium iodid.}}{2KI} + H_2O + \underset{\text{Ozone.}}{O_3} = \underset{\text{Potassium hydroxid.}}{2KOH} + \underset{\text{Iodin.}}{I_2} + \underset{\text{Oxygen.}}{O_2}$$

The least trace of free iodin can be detected by a solution of starch, which will turn a deep blue color. *Schönbein's test-paper* is made by saturating pieces of white filter-paper with a mixture of solutions of starch and potassium iodid. If dried and kept in tight bottles, this paper is a ready test for ozone in the air. To use it, the paper must be moistened with distilled water and suspended in an exposed place to the current of air to be tested. This test is liable to a fallacy from the fact that when either chlorin or nitrogen tetroxid is present iodin is liberated and the same color reaction ensues. Ozone, however, is peculiar in yielding the alkali potassium hydroxid, or KOH, of the equation given above. It is an improvement on Schönbein's method to apply *litmus* instead of starch to prove that the potassium iodid has been decomposed by ozone. A solution of potassium iodid colored with a reddish-violet litmus and exposed in a shallow white

dish for several hours will detect ozone in the air very readily. A control experiment should be conducted with the portion of the same litmus solution without the iodid. Another convenient method is to expose violet litmus-paper moistened with a solution of potassium iodid. If ozone be present, this test-paper will be turned blue from the alkaline hydroxid; but the same paper wet with distilled water will be unaffected.

Properties.—Ozone as a gas is bluish, having an odor like that of chlorin. It has been liquefied at $-105°$ C. ($-157°$ F.), with a pressure of 125 atmospheres, and is then of blue color. As ordinarily dealt with, it is always largely diluted with oxygen. In the dry state it can be kept unchanged, though its intrinsic energy gives it a tendency to explode into the state of ordinary oxygen, developing heat. At a temperature of 250° C. (482° F.) it is reconverted into oxygen. It is soluble in turpentine and sparingly so in water.

Its chief chemical attribute is that of an oxidizing agent. By it elementary phosphorus, sulphur, and arsenic are oxidized to acids, and ammonia to nitric acid. Metals that do not rust in the air, such as mercury and silver, soon lose their brilliancy in ozone. Only gold and the members of the platinum group resist it.

Paper made black with lead sulphid becomes white, the ozone changing the sulphid, PbS, to the white sulphate, $PbSO_4$. Organic substances, such as cork and rubber, are corroded by it; organic colors are bleached and gases of foul odor decomposed. It is a strong irritant to the air-passages, causing acute catarrhal symptoms even when the air contains so small an amount as 7 parts in the 100,000. At this concentration it is not disinfectant.

Nature of Ozone.—When oxygen is ozonized by exposure to electric discharges its volume is diminished and its density increased without the application of cold or heat, but when the ozone is heated to 250° C. (482° F.) it regains its volume while losing its characteristics as ozone. Three volumes of oxygen are condensed to form two of ozone; hence it is sometimes called *condensed oxygen* or *allotropic oxygen*.

Allotropism.—When an element presents itself in two or more different modifications, the property is termed allotropism. There are allotropic forms of oxygen, sulphur, phosphorus, carbon, iron, etc. To explain the fact of condensation when oxygen takes the form of ozone resort is had to the theory of the molecular constitution of matter. Matter is assumed to be composed of small separate particles called *molecules*, which are usually groups of two or more smaller particles, called *atoms*. Many facts sustain the *law of Avogadro:* "Equal volumes of elementary gases contain an equal number of molecules." The condensation of three volumes of oxygen to two of ozone is then accounted for by assuming that in an equal volume the ozone contains one-third more atoms,

which must be accommodated in the equal number of molecules by making the molecules heavier. If the molecule of oxygen is symbolized by O_2, then that of ozone becomes O_3. Three molecules of oxygen then contain six atoms in three groups of two each. When they change to two molecules of ozone, they contain the same number of atoms, but in two groups, containing three atoms each, $3O_2 = 2O_3$.

Carbon dioxid is produced when carbon is burned, whether in oxygen or ozone, but the number of the calories produced is very different in the two cases. More heat is given off by combustion in ozone than in oxygen—proof that the molecule of ozone has more *intrinsic energy*. Stated as an equation: Ozone = oxygen + energy. Allotropic elements may be regarded as those which under varying conditions take up different amounts of energy and thereby show a difference of properties.

In the equation below the facts are represented on the theory of molecules and atoms:

$$O_3 \rightleftarrows O_2 + O + 32{,}900 \text{ cal. } (137 \text{ kj}).$$

The O_3 represents molecular ozone which yields O_2, one molecule of ordinary oxygen, and O, one atom uncombined, said to be *nascent* oxygen, which has an extraordinary readiness for a chemical union. In terms of the molecular theory allotropism is the property of an element, under different circumstances, to appear in molecules which have a difference in their atomic constitution.

HYDROGEN

Symbol, H. Atomic weight, 1.008.

Occurrence.—Hydrogen exists free in the gaseous emanations from volcanoes, certain mines, "natural gas," and petroleum wells. As a product of fermentation of organic matter it is found in gastric and intestinal flatus. Its peculiar "lines" are seen in the spectra of the sun and various stars.

Combined with other elements, hydrogen is exceedingly abundant. With oxygen it forms one-ninth of the weight of all the water on the globe; with nitrogen it is present in the air as ammonia; with sulphur it makes the gas hydrogen sulphid, present in sulphur waters. In organic nature it occurs not only in the hydrocarbons and the carbohydrates, but in almost all animal and vegetable substances.

Preparation.—1. **By Electrolysis.**—If a current of electricity be passed through acidulated water by platinum electrodes pure hydrogen bubbles off at the negative pole and oxygen at the positive, two volumes of the former to one of the latter (Fig. 25).

The hydrogen is identified by its taking fire when lighted, the oxygen by its causing a glowing splinter of wood to burst into flame. The current is usually obtained from a battery of five or more galvanic cells—a combination of zinc and carbon plates immersed in a liquid that acts upon the zinc. The chemical action in the battery is transformed into electricity, which is transmitted by the conductors to the apparatus for electric decomposition. The process of separation of the constituents of a compound by electricity is known as *electrolysis*. By means of this process the most obstinate compounds have been resolved into their elements under the conditions stated on p. 50.

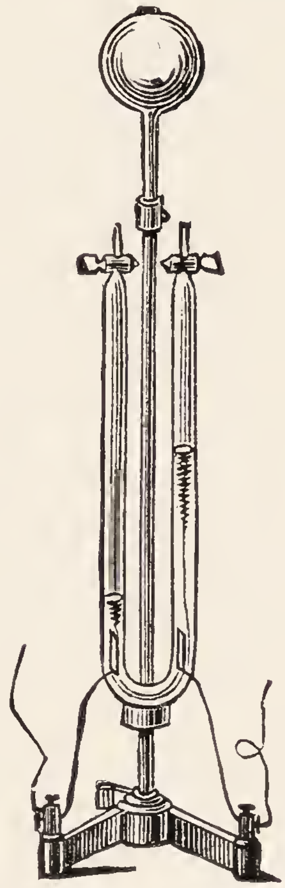


FIG. 25.— Apparatus for the electrolytic decomposition of water, yielding hydrogen and oxygen separately.

The substance must be a conductor of electricity—*i. e.*, an *electrolyte*. Pure water possesses this property in such an exceedingly small degree that it is regarded as a non-conductor. Its conductivity is improved by adding to it one-fourth part of sulphuric acid, which furnishes the *ions* necessary for conducting the current.

2. **By the Action of Various Metals on Water.**—The affinity of metals for oxygen can be used in the decomposition of water for liberating hydrogen. Most metals act very slowly at ordinary temperature, but potassium and sodium decompose water very promptly. They unite with oxygen with such violence that the free hydrogen is inflamed. A piece of potassium or sodium the size of a pea thrown upon water will float about (Fig. 26), first melting into a silvery globule, hissing hot, then glowing, and finally igniting the free hydrogen. If the water has been tinctured with red litmus, it will turn blue from the formation of sodium hydroxid.

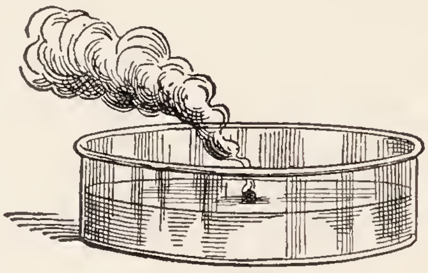


FIG. 26.—Potassium decomposing water.

$$\underset{}{H_2O} + \underset{\text{Sodium.}}{Na} = \underset{\text{Sodium hydroxid.}}{NaHO} + H.$$

In order to collect the hydrogen unignited a test-tube or glass cylinder should be filled with water and inverted with the open end immersed in a trough of water. Small pieces of sodium

wrapped in filter-paper can then be held by forceps underneath the mouth of the test-tube. The gas is given off and collects above the surface of the water, forcing the water out of the tube. To

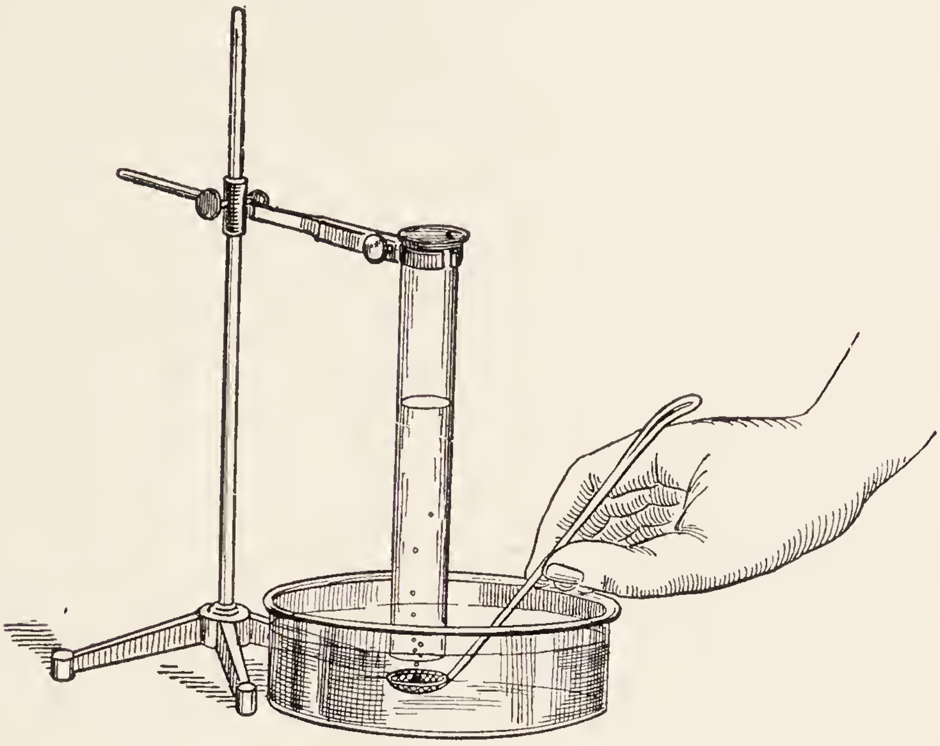


FIG. 27.—Hydrogen disengaged from water by sodium.

prevent explosions the sodium should be cut into pieces no larger than a split pea. In Fig. 27 the sodium is held under water by a wire-gauze spoon which permits the gas to rise into the cylinder. To moderate the violence of the action an alloy of 35 per cent. sodium with lead called "hydrone" is used in the laboratory. When immersed in water it yields pure hydrogen safely.

3. **To get hydrogen for manufacturing purposes** on a large scale the affinity of iron for oxygen is utilized. Here high heat is required. Steam is passed over iron turnings heated to redness in an iron tube.

$$\underset{\text{Iron.}}{3Fe} + \underset{\text{Water.}}{4H_2O} = \underset{\text{Iron oxid.}}{Fe_3O_4} + \underset{\text{Hydrogen.}}{4H_2}$$

The iron is oxidized to the tetroxid and the hydrogen passes out to the collecting apparatus. If charcoal be used instead of iron at a high heat, a gas, carbon monoxid, is formed, and the two gases can be utilized as sources of heat and light.

$$C + H_2O = \underset{\text{Carbon monoxid.}}{CO} + H_2.$$

4. **Hydrogen for the laboratory** is customarily prepared by the reaction of some acid upon a metal. The acids all contain hydrogen and have the common characteristic of giving it up easily, taking a metal in exchange. The most convenient materials are zinc and dilute sulphuric acid.

$$\underset{\text{Zinc.}}{Zn} + \underset{\text{Acid sulphuric.}}{H_2SO_4} = \underset{\text{Zinc sulphate.}}{ZnSO_4} + H_2.$$

Zinc sulphate remains in solution, and the hydrogen is set free. If hydrochloric acid be used, then

$$\underset{\text{Acid hydrochloric.}}{Zn + 2HCl} = \underset{\text{Zinc chlorid.}}{ZnCl_2} + H_2.$$

These reactions are illustrations of *substitution*. The zinc is substituted for the hydrogen, and there is a new arrangement of the elements (Fig. 28).

To perform this operation the zinc, in small pieces, is put into a glass flask or two-necked bottle. The stoppers of rubber or cork are perforated for tubes. One has a funnel outside, the lower end reaching nearly to the bottom of the flask. The other tube is short within the flask and bent outside at an angle convenient for the attachment of a delivery tube. When the apparatus is tightly closed the sulphuric acid, diluted with five to six

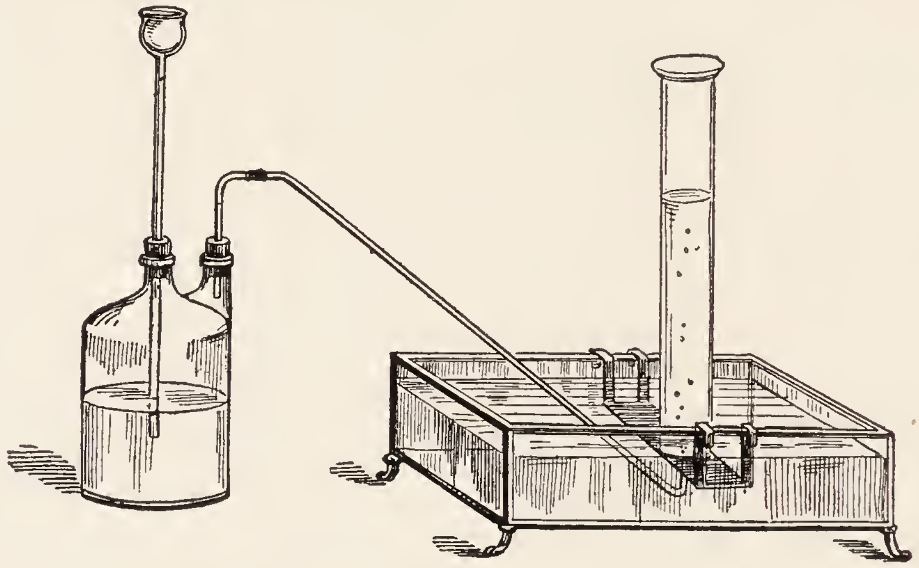


FIG. 28.—Hydrogen generator.

parts of water, is poured through the funnel tube and a brisk effervescence begins immediately. The gas bubbles through the water of the pneumatic trough and collects in jars prepared for receiving it.

Precaution.—Before collecting, it is advisable to allow sufficient gas to escape to be sure that the air has all been expelled from the collecting jars, otherwise an inflammable mixture is formed which, when ignited, explodes with dangerous violence. The test for this consists in obtaining a sample of the hydrogen at the trough by inserting a water-filled test-tube over the escaping bubbles. Pure hydrogen burns quietly at the mouth of the tube held mouth downward, while the occurrence of a slight explosion proves that some air still remains.[1]

Physical Properties.—Hydrogen is the lightest known sub-

[1] Prepared in this way from common zinc the gas always has an odor, due to the formation of gaseous compounds of hydrogen with arsenic and phosphorus present in the impure zinc, or to hydrogen sulphid when hot acid is used, or to nitrous and nitric oxids when the acid contains some nitric acid.

stance, being 14.47 times lighter than air. Its specific gravity is 0.06926 (air = 1), and 1 liter weighs 0.0899 gm. It is transparent, colorless, odorless, and tasteless. It is not poisonous, but will not support life. If permitted to escape from a pressure of 180 atmospheres at −205° C. (−337° F.) it is a colorless, clear liquid, which freezes by its own evaporation, reaching a temperature of −258° C. (−432.4° F.). It is nearly insoluble in water. It conducts heat and electricity better than any other gas. It is the most highly diffusible of gases, passing through a porous medium four times more rapidly than oxygen. Gas-bags of rubber, leather, membrane, or other porous material permit this diffusion with such freedom that in a short time the contents of the bag become an explosive mixture, consisting of hydrogen and oxygen obtained from the air.

If the metal palladium is used as the negative electrode in the electrolysis of water, 980 volumes of hydrogen will be retained by it. By applying heat the metal gives up this *occluded* gas in a very active condition, similar to the state of hydrogen just free from chemical combination.

Chemical Properties.—While hydrogen and oxygen resemble one another in physical properties, chemically they are opposites and have a great attraction for one another. Hydrogen, however, is unique in its affinities, resembling the metals more than the non-metals, combining with chlorin, nitrogen, sulphur, and carbon. It does not support combustion, but burns with a non-luminous blue flame, hotter than that produced by any other burning substance in equal weight. In combustion two volumes of it unite with one volume of oxygen to form two volumes of water vapor. If the gas be dried, by passing it through a desiccating tube, and then ignited at the terminal jet (Fig. 29), it burns with a pale flame, depositing moisture on the glass bell-jar. Mixed with chlorin, hydrogen explodes in the sunlight; with oxygen it explodes violently by the touch of a flame or an electric spark.

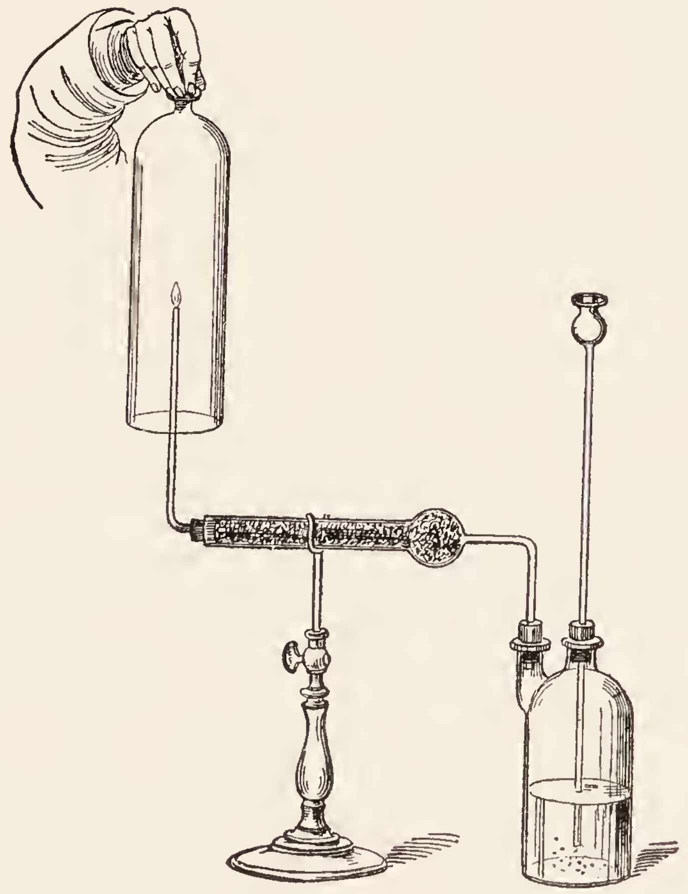


Fig. 29.—Water formed by burning hydrogen.

In the oxyhydrogen blowpipe a blast of oxygen is blown through the hydrogen flame; at its temperature of 2000° C. (3632° F.) quartz and ruby are fused. The lime light for stereopticons is made by heating lime in it to incandescence.

Hydrogen is a *reducing* or *deoxidizing agent.* That is to say, it will take oxygen from oxids, reducing them to lower oxids or to the metallic state. Copper oxid or iron oxid at a red heat in a stream of hydrogen parts with the oxygen, forming water and the free metal:

$$Fe_3O_4 \quad + \quad 4H_2 \quad = \quad 4H_2O \quad + \quad 3Fe.$$

Reversible Processes.—Red-hot iron oxidizes in steam; the water giving oxygen to the iron is reduced to hydrogen. On the other hand, to produce the purest form of iron, such as is used in medicine under the name *reduced iron*, hydrogen is passed over red-hot iron oxid (p. 79). This mutual play, by which substitution and reformation can be made to occur at will, is expressed in an equation which can be read either way, the double arrow meaning that it is reversible:

$$\text{water} \quad + \quad \text{iron} \quad \rightleftarrows \quad \text{hydrogen} \quad + \quad \text{iron oxid.}$$

In any chemical process we must consider not only the affinities and the temperature of the substances, but also another influence, the active *mass* or *concentration*, or, to state it more accurately, the ratio of substances present. If the amount of hydrogen is relatively large the equation should read from right to left, but if the ratio of water vapor predominates in amount the reading is reversed. To use a homely illustration: a man may carry a pail of water, but a flood of water will carry away the man.

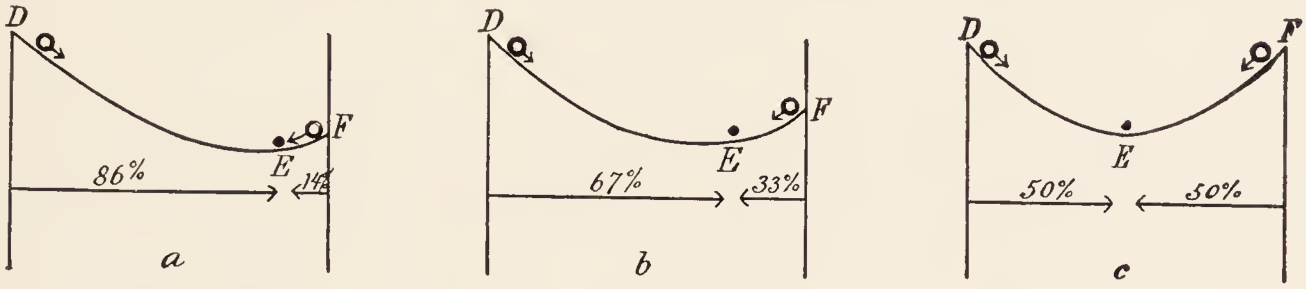
Mass-action.—This is defined as *that effect upon the chemical interaction of substances due to their relative masses,*—*i. e.*, to the number of acting molecules in unit volume.

When the operation is conducted in an apparatus that does not permit the escape of the hydrogen nor the condensation of steam to water, the oxidation of iron by water vapor touches its maximum when a definite ratio is reached between the hydrogen and the water vapor present. This ratio is the same as that established by the reverse process of reducing iron oxid by hydrogen (Fig. 30, *c*).

Chemical equilibrium is the state of apparent balance caused when two opposing movements equalize each other. This obtains in all chemical processes, although in many the balanced concentrations of some of the substances engaged are so small as not to be noticed,

the observer detecting the movement in one direction only (pp. 37, 43, and 134).

The usual terms employed to describe a chemical reaction are based upon the theory of an impelling force causing one element to drive another out. It is more satisfactory to discover the position of equilibrium by calculating the ratios of opposed forces and then state them as relative velocities. When the velocities of two opposite reactions are equal, so that in a unit of time each acts as much as the other, we have the condition of equilibrium. In the diagram (Fig. 30) it is shown that the point of equilibrium may be



Maltose changing to glucose (p. 439). | Formation of ethyl acetate. | Reduction of Fe_3O_4.

FIG. 30.—Equilibrium of opposing reactions; the vigor is indicated by the height of the lines *D* and *F*, and the velocities by the arrows.

attained at different degrees of concentration of the materials, dependent on the initial vigor of the opposing reactions.

The velocities are indicated by the length of the arrows. The balls rolling down the inclines show at *E*, the point when chemical change appears to cease, leaving some of the original *factors* present with the new *products*. In *b* is shown acetic acid acting on ethyl alcohol at *D*, producing ethyl acetate and water at *F* (p. 434). The point of equilibrium is reached when 67 per cent. of the material has been transformed. The ester formation is represented by the motion along *DE*, the reverse hydrolysis by *FE*.

WATER

Formula H_2O. Molecular weight, 18.

Occurrence.—In nature it exists as a solid in snow and ice; as a liquid it forms lakes, rivers, and seas; suspended in the air as minute liquid particles it forms the clouds and fog; as a colorless gas it is a constituent of the atmosphere. It comprises three-fourths or four-fifths of the substance of plants and animals, and is found in various minerals, as *water of hydration* or of *crystallization*, where it is indicated by the sign of a comma before H_2O, as in the formula for sodium carbonate: $Na_2CO_3,10H_2O$. The water thus combined in crystals is in definite proportions, is always necessary to their form, and often to their color, but does not affect their chemical relations. A crystal which, like sodium carbonate, gives off this water spontaneously is said to *effloresce*.

Salts which, like calcium chlorid, absorb water from the air and dissolve are said to *deliquesce*, thereby forming *hydrates*.

A solid hydrate when heated loses its water and crumbles into the *exsiccated* form without losing its chemical properties.

Formation.—It has been stated before that by electrolysis of water two volumes of hydrogen are evolved at the negative electrode and one volume of oxygen at the positive. If these three volumes be introduced into an *eudiometer*[1] (Fig. 31), they will explode by a spark and unite to form two volumes of the vapor of water when measured at 100° C. (212° F.).

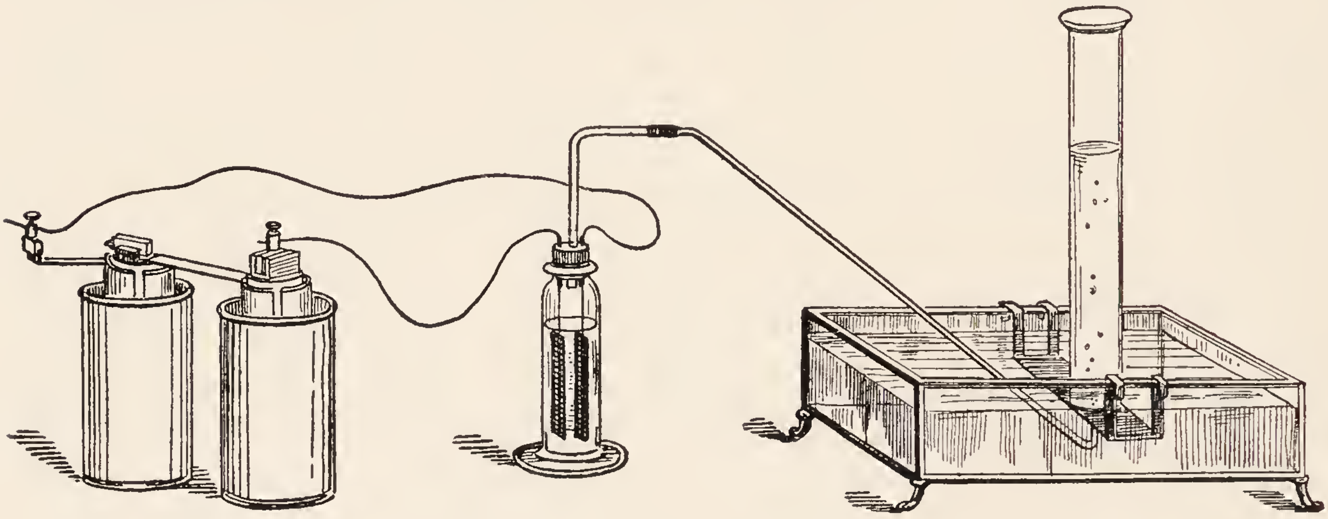


Fig. 31.—*A*, Battery; *B*, electrolytic cell; *C*, mixed gases, explosive.

Physical Properties.—Without taste or odor, water appears colorless in ordinary vessels, but it is bluish green when observed in layers several yards in thickness. Its freezing-point is 0° C. (32° F.), its boiling-point 100° C. (212° F.). It is a poor conductor of heat, but may be heated readily in masses from below through the circulation of *convection currents*. It contracts when cooled until the temperature is lowered to 4° C. (39.2° F.), at which point it reaches its *maximum density*. This property is the opposite of that possessed by most substances, where the withdrawal of heat means contraction indefinitely. From 4° C. (39° F.) down to 0° C. (32° F.) water expands as it cools (one volume becoming 1 + 0.00012). In freezing as ice it becomes specifically lighter and floats on the liquid water. This explains the fortunate circumstance that lakes, rivers, and seas in cold latitudes do not freeze solid from the bottom up. Under the surface-ice the water keeps at a temperature compatible with the life of the aquatic inhabitants. Winds cool the surface-water, which, becoming heavier, sinks, and lighter and warmer water rises to its place. This goes on until the whole is reduced to 4° C. (39.2° F.), and then the surface-water no longer sinks. Ice is

[1] An eudiometer is an instrument for analyzing gases by exploding out the hydrogen with oxygen, or *vice versa*, and measuring the calm gases left.

formed only at the top, the mass of water retaining a temperature of 4° C. (39.2° F.). If water became heavier as it cooled down to the freezing-point, a continual circulation would be kept up until the mass was cooled to 0° C. (32° F.), when solidification of the whole would take place.

Most of the soluble solids dissolve in water. Being neutral, it takes on the properties of dissolved substances in odor, color, taste, or chemical reaction, acting simply as a vehicle. Natural waters vary in the character and amount of these constituents because of the difference in the rocks and soils from which they have been extracted. Beyond a certain proportion the minerals give it an unwholesome quality, and then the water is not considered potable, but is called a *mineral water*. If it be highly charged with gases, it is said to be *effervescent*. *Sulphur water* contains the gas hydrogen sulphid. *Chalybeate* waters have iron salts in solution (p. 257).

Natural water is never chemically pure: even in the cloud or rain-drop it has taken up gases or dust from the atmosphere. By the term *aqua* (U. S. P.) is meant the purest attainable in a natural state. To get it free from impurity it must be distilled.

Distillation.—It is first changed into steam by heat and then the steam is cooled again until it condenses to liquid water. The impurities that are not volatile are left behind. The operation may be conducted in the *condenser* shown in Fig. 77. A current of cold water circulates in an outer jacket around an inner tube for steam. The hot vapor flowing down loses its heat to the cold water streaming up, which absorbs it, the two opposing currents tending to an equilibrium of temperature.

Sublimation.—When the distilled substance is a crude solid like native "brimstone," which is recovered as a purified solid like sulphur, the substance vaporized by heat is temporarily dissolved in the air and is said to be *sublimed*.

Aqua destillata (U. S. P.) is prepared by distilling 1000 parts of water, throwing away the first condensation of 100 parts as likely to contain dissolved gases such as ammonia; saving the next 800 parts, and leaving the last 100 parts in the retort lest the thickened fluid in boiling should spray over its salts.

Atmospheric Water.—Beside the visible forms of cloud or fog, the moisture of the air exists as an invisible vapor. The actual presence and amount of this water may be shown by sending the measured air through a *drying tube* containing calcium chlorid; the salt grows moist and increases in weight. A given volume of air is found to hold amounts of water vapor varying with the pressure and temperature. While some moisture is always present, it rarely happens that the air is saturated, commonly the

moisture present reaching only from 50 to 70 per cent. of the maximum.

By cooling the air sufficiently a temperature is reached at which the aqueous vapor has the pressure of its saturation-point. The slightest decline now causes the vapor to condense as *dew.* This temperature is known as the *dew-point.* A *hygrometer* is an instrument constructed to determine the amount of moisture in the air. The one commonly used consists of two thermometers, one dry, while around the bulb of the other is wrapped a cotton wick kept wet by one end dipping in a vessel of water. The wet bulb, by evaporation, indicates a lower temperature than the dry-bulb instrument. The rate of evaporation is the cause of the difference, and this depends on the amount of moist vapor and the temperature. If the difference between the instruments be great the air is dry, if slight the air is moist. By means of tables these factors can be converted into *relative humidity.*

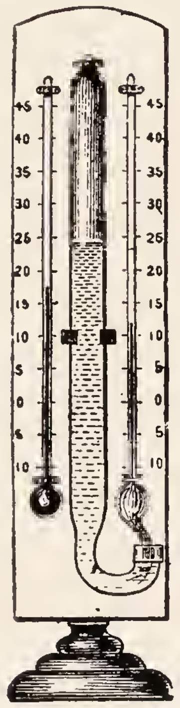


FIG. 32.—Wet- and dry-bulb hygrometer.

Relative humidity is a term applied to this fraction of full saturation for the air at existing temperature and pressure. *Relative humidity of* 100 means that the air is saturated, and that water will be precipitated should the temperature or pressure decline. An increase of temperature or pressure would raise the capacity of the air as a solvent, and the relative humidity would fall. Less than 50 per cent. makes the air dry; with more than 70 per cent. it is humid and depressing to the vital powers.

HYDROGEN DIOXID OR PEROXID

Formula, H_2O_2. Molecular weight, 34. Specific gravity, 1.455.

A trace of hydrogen dioxid is found in saliva, in the air, in snow, and in rain-water.

Preparation.—Dilute mineral acids acting on barium dioxid will produce hydrogen peroxid mixed with water.

$$\underset{\text{Barium dioxid.}}{BaO_2} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Barium sulphate.}}{BaSO_4} + \underset{\text{Hydrogen dioxid.}}{H_2O_2}$$

Sodium perborate is decomposed by water yielding sodium metaborate and hydrogen dioxid in solution.

$$\underset{\text{Sodium perborate.}}{NaBO_3} + H_2O \longrightarrow \underset{\text{Sodium metaborate.}}{NaBO_2} + H_2O_2.$$

In a concentrated form for use as a bleaching agent it is obtained by the action of dilute acids on sodium peroxid.

$$\underset{\text{Sodium peroxid.}}{Na_2O_2} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Sodium chlorid.}}{2NaCl} + H_2O_2.$$

Water becomes a source in dissolving sodium peroxid.

$$2H_2O + Na_2O_2 = 2NaHO + H_2O_2.$$

Properties.—When pure hydrogen peroxid is a syrupy liquid without color or odor, but with a metallic taste, and having a tingling effect on the mouth. It is soluble in water, alcohol, and ether in all proportions. The pure form decomposes readily into water and oxygen at ordinary temperatures, more rapidly at higher temperatures. Practically it is oxidized water.

$$H_2O_2 \rightleftarrows H_2O + O + 23{,}100 \text{ cal. } (96 \text{ kj}).$$

It may give off 475 volumes of oxygen, while the ordinary dilute form yields about 10 volumes. When diluted and slightly acidulated it is much more stable and may be concentrated to an extreme degree by careful evaporation under 60° C. (140° F.) without decomposition.

Catalytic Reactions.—When concentrated hydrogen dioxid comes in contact with certain metals, as platinum or certain oxids, as manganese dioxid, it breaks up explosively into water and oxygen. A piece of spongy platinum, when immersed in dilute hydrogen dioxid, becomes enveloped in a layer of oxygen gas. Removing this layer of oxygen another layer forms, and so on, until the dioxid is to a great degree decomposed, the platinum remaining unaffected.

Catalysis is chemical action as affected by the presence of a substance which does not itself enter into the reaction. A *catalyzer* is a body which, without appearing as an end-product in a chemical reaction, alters its velocity. While in most cases the catalyzer hastens the change, "positive catalyzers" some bodies, like hydrocyanic acid, inhibit action, and hence may be called "retarding catalyzers." The agent usually appears to act much as a lubricant does on machinery—that is, it accelerates a movement which would otherwise occur much more slowly if at all, the lubricant itself not being consumed in the process.

The Energy of Hydrogen Dioxid.—To decompose water, H_2O (a stable substance), it requires a strong electric current or very high temperature. Hydrogen dioxid, H_2O_2, with its additional atom of oxygen, acquires instability in a high degree. In

giving up that oxygen *a large amount of heat is liberated.* Each molecule of the dioxid holds that much more intrinsic energy than the molecule of water to which it is converted. This *intrinsic energy* gives it high instability and chemical activity in proportion.

Aqua hydrogenii dioxidi, U. S. P. (*oxygenated water*), is a solution in water of about 3 per cent. by weight of the dioxid corresponding to about 10 volumes of available oxygen. Without color or odor, it has a peculiar, feebly sour taste, denoting its character as acid. Mixed with saliva it evolves oxgyen, as it also does when mixed with pus.

To prevent spontaneous deterioration and explosive expulsion of the stopper it is best kept uncorked in a refrigerator. By means of glycerin a more stable solution is prepared. A solution in ether is called *ozonic ether.*

Uses in the Arts.—As an oxidizing agent it has quite remarkable bleaching powers, which are employed in bleaching hair, ostrich feathers, and wool. Books and engravings stained by mould and time are safely cleaned by it.

Uses in Medicine.—It is an antiseptic, destroying bacteria; a deodorant, decomposing hydrogen sulphid; and a styptic, coagulating the blood. It is of great service as a topic application to the throat in scarlatina and diphtheria, or as a disinfectant lotion for abscesses and wounds. When internally administered in doses of f℥j–iv, well diluted, care should be taken that the solution be free from barium and hydrofluoric acid. The small amount of free acid, if present, may be neutralized with a sufficient amount of sodium bicarbonate. It is given by the mouth as an antidote to the cyanids and the alkaloids.[1]

With hydrocyanic acid it forms *oxamid;* hence, if potassium cyanid has been taken, a tablespoonful of vinegar must be added to liberate the acid from the cyanid.

$$\underset{\text{Hydrocyanic acid.}}{2HCN} + H_2O_2 = \underset{\text{Oxamid.}}{C_2O_2N_2H_4}$$

Not only is the stomach flushed with the dioxid diluted, but 15 m. of the official preparation are also injected subcutaneously every ten minutes until respiration improves.

Incompatibles.—To arsenic and the sulphids, hydrogen peroxid supplies oxygen, but it reduces many compounds, like

[1] Solutions of potassium permanganate and hydrogen dioxid when mixed, reciprocally promote their yield of oxygen. The official 3 per cent. H_2O_2, about 35 cc. diluted with a liter of water, when mixed with a solution of potassium permanganate, 2 gm. in 5 cc. of diluted acetic acid to a liter of water, produces at once energetic disengagement of oxygen. They should be kept separate until needed and brought into contact only at the site of the disease; as antidotes, the above dioxid solution should be given in doses of a tablespoonful first and followed each time by an equal amount of the permanganate.

manganese dioxid, silver oxid, and potassium iodid. Many substances in a state of fine division, acting by catalysis, cause hydrogen dioxid to lose its oxygen. Among such substances are included all the ferments or enzymes, ordinary dust, powdered charcoal, fibrin, platinum, and gold. Hydrogen dioxid is also decomposed by albumin, ammonia, iodids, chlorids, bromids, chlorin-water, solution of chlorinated soda, carbolic acid, ferric salts, hydrocyanic acid, lime-water, the permanganates, and alcoholic tinctures.

Tests.—(1) *Starch and Iodids.*—A few drops of a solution of potassium or cadmium iodid are added to a cold solution of starch acidulated with acetic or citric acid. Then the fluid to be tested is added. Hydrogen dioxid, even in the presence of ferrous sulphate, produces a blue color, liberating free iodin, which unites with the starch. Other oxidizing agents liberate iodin, but not in the presence of ferrous sulphate.

$$2KI + H_2O_2 = 2KOH + I_2.$$

This test will show hydrogen dioxid when there is present only 0.05 mgm. per liter.

(2) *Perchromic Acid.*—When acidulated with dilute sulphuric acid, hydrogen dioxid will cause potassium dichromate to form blue perchromic acid—$4CrO_3$. By shaking with ether and setting aside, the product separates as a supernatant transient violet-blue layer. No other substance oxidizes chromic to perchromic acid.

SOLUTION. DIFFUSION. DIALYSIS. OSMOSIS

SOLUTION

Some solids when immersed in water disappear in it, imparting to the liquid their own properties, such as color, odor, and taste. They assume for the time being the liquid state. A *solution* of sugar is sweet, and of salt brackish, the chemical behavior being that of the original solid. The particles of the *solute* are diffused so evenly in the *solvent* that every part of the liquid contains equal amounts dissolved in it. One grain of fluorescin or uranin will render fluorescent or will color one hundred million grains of water. The original grain has been divided infinitely in the process of absorption by water.

Solutions are homogeneous mixtures of two or more elements or compounds which cannot be separated mechanically.

Solutions of Solids in Liquids.—It is a general rule that some portion of a solid, albeit infinitesimal, always dissolves in a liquid in contact with it. A trace of platinum dissolves in water. This is not the only form of solution, but, being the most familiar, the word *solution* is taken to mean the solution of a solid in a liquid. As though it were a chemical effect, there is a limit to the amount of any solid dissolvable in a certain amount of any liquid. This limit depends upon the nature of the solvent, the nature of the *solute*, and the temperature.

As more substances are freely soluble in water than in any other liquid, we speak of the solubility of a substance without naming the solvent, meaning water. Water, however, is not a good solvent for a large number of solids—like the resins, which dissolve freely in alcohol; phosphorus, soluble in ether; sulphur, soluble in carbon bisulphid; and gutta-percha, soluble in chloroform. While theoretically all solids are said to be soluble in water, to some degree discoverable by physical tests, the amount of gold and other metals, quartz and many other minerals, is so small as not to be discovered by chemical tests. These substances are considered to be practically insoluble, while the contrary is the case with many metallic salts, acids, alkalies, sugars, and a host of organic products. The solubility of some of these is very great, yet in the extremest case there is a limit beyond which it is not possible to dissolve a solid in a liquid. This limit, constant at any given temperature, is the *point of saturation*. The solution is said to be *saturated*. In making a saturated solution it will be found a great help to have the solid pulverized and stirred or shaken with the solvent. Practically this method is not so rapid as one based upon the fact that solubility of most substances rises with the temperature. Thus, at 0° C. (32° F.), 100 parts of water dissolve 26 parts of magnesium sulphate; at 40° C. (104° F.), 45 parts; at 100° C. (212° F.), 74 parts. The *concentration* of a solution means the amount of the *solute* in a given quantity of the *solvent*.

After having made a saturated solution of a calcium salt at ordinary temperatures, if heat be applied, the effect is the precipitation of the salt. Common salt is almost equally soluble at all temperatures. With the great majority of solids, such as sugar and alum, if hot water be used to make the solution and a large quantity of the solid be shaken with it, when the solution cools the excess dissolved at the higher temperature will be thrown out and a saturated solution be left. Sometimes the clear liquid may be cooled without throwing out all excess. Thus we may get a solution which at any given temperature holds more of the solute than a simple saturated solution. The equilibrium is not stable

because agitation with a crystal of the undissolved substance will cause the excess of the solid in solution to be deposited. The *supersaturated solution* is thus converted into a saturated one.

If sodium sulphate be dissolved by aid of heat and the clear liquid free from undissolved particles be allowed to cool quietly, excluding dust, a crystal of the same salt dropped into the supersaturated solution causes immediate crystallization with elevation of temperature.

While the dissolved substance can not be separated by mechanical means, it may by evaporation of the liquid. The solute is not carried over in the vapors, but is recovered unchanged.

Solutions of Gases in Liquids.—All liquids possess the power (though it may be infinitely small) of absorbing all gases. The amount absorbed varies with the nature of the liquid, the nature of the gas, the temperature of the solvent, and the pressure on the gas. At 0°C. (32° F.) a liter of water dissolves only half as much carbon dioxid as an equal volume of alcohol.

It has been previously stated that oxygen, hydrogen, nitrogen, and air are soluble in water to a slight extent only. We shall learn that chlorin and hydrogen sulphid are more soluble, while hydrochloric acid and ammonia are absorbed by water in large amounts.

The extent of solubility is much influenced by temperature and pressure. As the *temperature* rises the amount of gas dissolved decreases. At 10° C. (50° F.) 100 volumes of water will hold in solution 110 volumes of nitrous oxid; when heated to 20° C. (68° F.) much gas escapes, leaving only 67 volumes.

The relation of *pressure* to solubility is expressed in *Henry's law: The amount of a gas absorbed by a liquid is directly proportional to the pressure to which the gas is subjected.* Thus, under a pressure of five atmospheres, water dissolves five times as much carbon dioxid as under a pressure of one atmosphere.

Solutions of Liquids in Liquids.—These belong to one of two classes: first, where the liquids mix in all proportions homogeneously, as alcohol and water; second, where they dissolve in each other to a limited extent only, as ether and water. Theoretically, all liquids are soluble in each other to at least an infinitesimal degree, but, practically, there are liquids which are not miscible, such as oil and water.

When liquids are freely miscible, the mixture often has properties representing the sum of those of the components, though they are never strictly *additive.* In most cases there is a change of volume; usually the mixture shrinks, but sometimes it increases. In most cases there is a change of temperature which may be

either a rise or a fall. When alcohol is mixed with water a contraction of volume occurs and the temperature of the mixture rises.

When liquids are miscible to a limited extent only, the properties of the mixture can not be assumed to be the sum of the constituents. When there is an excess of one liquid and a mechanical separation, it will be found that each separate liquid has dissolved a different amount of the other. If equal volumes of ether and water be shaken together and set aside, they will soon form two layers. The upper layer of ether contains 2 per cent. of dissolved water; the lower layer consists of water holding 10 per cent. of the ether dissolved in it. It can be stated that the mutual solubility is limited only at ordinary temperatures. By heating, the liquids will at last reach a point where they become miscible in all proportions.

Solutions of Gases in Gases.—When two gases in contact do not unite chemically, they diffuse into one another, making a uniform mixture, as the nitrogen and oxygen of the air. There is no limit to the capacity of a gas to dissolve another, the resulting mixture having the combined properties of the components. The pressure of the mixture equals the sum of the pressures of the constituents (see p. 41).

Solutions of Liquids in Gases.—Generally speaking, liquids will evaporate into surrounding gases. The gas dissolves the liquid with such freedom that the vapor-pressure of the evaporated liquid is the same as it would be in a vacuum (see p. 39).

Solutions of Solids in Gases.—Certain solids, such as iodin, without being first liquefied, pass into the state of vapor and dissolve in the air or other gases. The solubility increases with rise of temperature.

DIFFUSION

Diffusion of Gases.—In the section that treats of hydrogen (page 81) it was shown that a gas passes through the porous walls of a cell much faster than the air passes out. If the experiment be repeated with air outside and carbon dioxid inside, a similar effect is produced, the lighter gas diffusing more rapidly than the heavier.

Graham's law states that *the velocities of diffusion of any two gases are inversely as the square roots of their densities.* Oxygen weighing 16 diffuses one-fourth as fast as hydrogen weighing 1; chlorin weighing 36 diffuses at one-sixth the rate of hydrogen. This follows from the *kinetic theory of gases*, which assumes that the mean velocities of the molecules of gases are inversely proportional to the square roots of their densities.

Diffusion of Liquids.—If a cylindric vessel be partly filled with water and the water underlaid with a colored solution (a sat-

urated solution of copper sulphate), by pouring the latter solution through a long funnel reaching to the bottom of the vessel two well-defined layers will be formed. If the cylinder be set aside for a few days it will be seen that the blue color has risen gradually and extended into every part of the water, making a uniform tint throughout. Chemical analysis will prove that the copper salt has distributed itself equally throughout the solvent, making a homogeneous solution. Likewise two solutions of different substances will diffuse into each other until there is but one homogeneous mass. Moreover, regardless of the weight of the dissolved substance, the solution maintains this property of uniform distribution indefinitely. The force of diffusion overcomes the counteracting force of gravity.

From an extended series of experiments Graham deduced the following conclusions: The quantities of a dissolved salt which diffuse in equal times are proportional to the concentration of the solution, and to the rise in temperature.

Different substances have different rates of diffusion, cane-sugar diffusing with seven times the velocity of albumin. Isomorphous salts frequently show equal rapidity. A double salt, such as alum, may be resolved into its components by means of their unequal velocity, the more diffusible part moving away at a greater rate.

DIALYSIS

If a drum of glass open at both ends be closed at one end with a stretched membrane, such as bladder or parchment, then floated on water, and a mixture of substances, such as sugar and albumin, placed in it, a remarkable separation of the sugar and albumin occurs. The sugar passes out through the membrane, while the albumin remains behind.

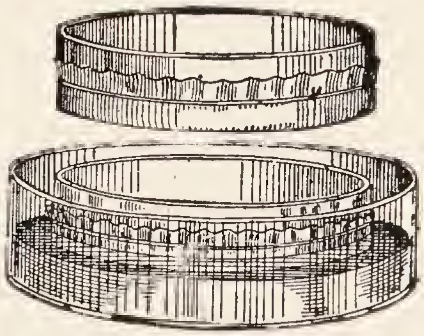


Fig. 33.—Graham's apparatus for the application of dialysis.

This process of separation is known as *dialysis*, the instrument is a *dialyzer*. The crystalline substance separated is the *dialysate*. Graham divided all substances into two classes: *crystalloids*, those which diffuse and are also crystallizable; *colloids*, those which are unable to pass through the membrane and which are also amorphous, like gum or glue. To the class of crystalloids belong sugar, the mineral salts, and acids; to the colloids belong albumin, gelatin, starch, and gum. Crystalloids have molecules sufficiently small to pass where the larger molecules of the colloid can not readily move. In some cases relatively small *molecules* appear to cling together to form *solution aggregates* which can not diffuse. Some of the metals—platinum, gold,

and silver—can be obtained in a condition known as colloid solution. A strong electric current is sent through water by platinum electrodes with tips close enough to make an electric arc. Minute particles of platinum are torn off in *aggregates*, making a brown solution which does not dialyze, and hence is called *colloidal*. Viewed by the ultramicroscope, the "solution" proves to be a suspension of shining metallic particles. Such a solution has the catalytic power of a ferment on sugar and fat (p. 544).

OSMOSIS

If a dialyzer full of molasses or brine be immersed in water it will be noticed that the contents of the inner vessel increase and the membrane appears to be forced up. If instead of a cylindric drum a long-stem funnel be used (Fig. 34), stretching the parchment over the head of the funnel, *b–a*, we have an *osmometer*, or apparatus for observing the phenomenon of the transmission of liquids, which causes the level of the fluid to rise as in tube *n*. We have seen that the passage of a dissolved substance is called *dialysis;* when the passing molecules are those of the solvent it is termed *osmosis*. There is in reality an interchange, but more molecules of water stream *into* the brine than of salt *out* to the water.

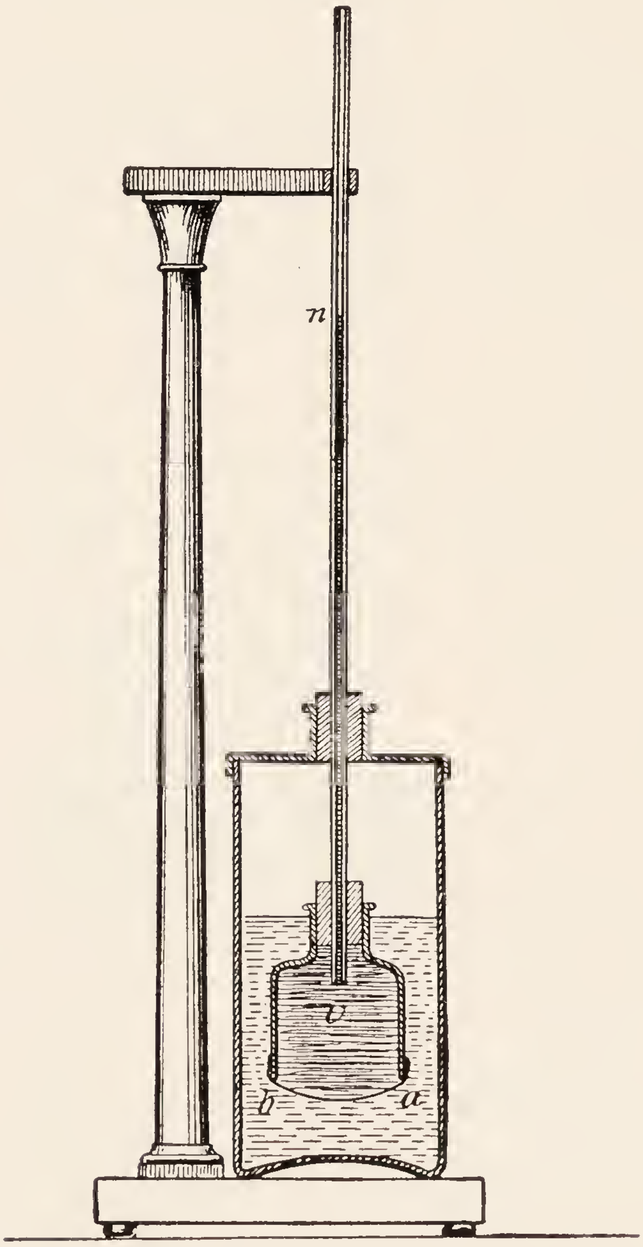


Fig. 34.—Endosmometer: *a–b*, porous membrane; *v*, diffusate risen to *n*.

A better medium for showing this pressure of the water toward a solution of salts is the *semipermeable membrane of Pfeffer*, made by precipitating gelatinous copper ferrocyanid within the pores of a membrane or the walls of a porous cell. This is permeable to the water, but not to the dissolved substance; it is not a dialyzer. When a solution of cane-sugar is put inside of an osmometer with this artificial membrane separating it from water, the *osmotic current* is

toward the sugar, v, no sugar passing out. In their futile efforts to push on out toward the water the sugar molecules exert a pressure which is toward all the boundaries of the cell, including the free surface of liquid in the tube n. The free surface of any liquid behaves like a thin film or movable partition.

It moves upward, enlarging the volume of fluid in the cell, making easier the entrance of water through the membrane. This movement causes the level of water in the stem to rise to a certain point, when the pressure reaches an equilibrium with the weight of the column of fluid. This highest degree of pressure is known as the *osmotic pressure* of the solution. If the semipermeable cell be filled with a normal solution of cane-sugar, and the stem be a capillary tube, pure water will press in so fast that the liquid in the tube rises more than a foot an hour, and in a day will reach a pressure of thirty feet of sugar solution. By connecting to the cell a tube of the form used for manometers, we can calculate the pressure in exact terms.

Osmotic pressure is that push of the molecules of a solute upon its solvent which causes a flow through a membrane into the solution. Its laws are:

(1) At a constant temperature the osmotic pressure is proportional to the concentration of the solution.

(2) With a given solution it is proportional to the absolute temperature.

(3) Under constant conditions of concentration and temperature different substances in solution exert different pressures.

(4) The molecular weights in grams per liter of different substances exert the same pressure at the same temperature.

These laws resemble closely those stated as governing the pressure of gases in confined spaces (see p. 40). The osmotic pressure, like the gas pressure, varies with the concentration, and increases $\frac{1}{273}$ for every rise of 1° C., or $\frac{1}{491}$ for every 1° F.

According to the *law of Avogadro*, equal volumes of all gases at the same temperature and pressure contain the same number of molecules. So in equal volumes of solutions having the same osmotic pressure there are the same number of molecules. The osmotic pressure of a solution of cane-sugar is exactly equal to the gas pressure of a gas with the same number of molecules in a given volume. The gas pressure exerted by a gas molecule equals the osmotic pressure of a dissolved molecule. These laws do not apply to the osmotic pressures of most salts, all the strong acids, and all the strong bases, which are always greater than the laws would lead us to expect.

To solve the problem presented by so many exceptions, the theory of *ionization* or *electrolytic dissociation* is needed. If the acids, bases, and salts exert abnormal osmotic pressure they must

have more dissolved particles than can be accounted for by their molecules. Let us suppose that the theory given (p. 52) to explain electrolysis be true—that is, that in making solutions of salts, acids, and bases there is a partial breaking up of the molecules, not into free atoms, but into electrically charged parts called *ions*, which may be charged atoms or charged groups. In this way we can conceive of more particles than are accounted for by the molecules. According to the method of Arrhenius the percentage of molecules broken down into ions can be calculated. When this is done, there is found the right proportion of *particles*, *i. e.*, molecules plus ions, to bring the exceptional substances under the reign of the laws above stated.

Osmotic pressure being the push of the particles of a solute, it tends, in proportion to their number, to impede that free movement of the molecules of the solvent which is necessary to arrange them anew for the frozen state. For instance, solutions of equal osmotic pressure have also the same freezing-point. Freezing-point depression in a solution is proportional to the number of particles dissolved. The amount of freezing-point lowering of any normal (gram-molecular) solution in water has been stated to be the constant 1.87 (p. 38).

Therefore, the osmotic pressure of a solution can be calculated by dividing 1.87 into the amount of lowering of the freezing-point of that solution in Centigrade degrees (its Δ—delta). Blood-serum freezes 0.56° C. below the freezing-point of pure water. 0.56° C. divided by 1.87 gives 0.3. Now the constant osmotic pressure for normal solutions of undissociated substances is 22 atmospheres; therefore, 22 multiplied by 0.3 gives 6.6 atmospheres as the osmotic pressure of blood-serum. A solution of a salt having the same osmotic pressure as blood-serum is said to be *isotonic* or *isosmotic*, such as 0.95 per cent. sodium chlorid. A solution of higher pressure is said to be *hypertonic;* one of lower, *hypotonic*.

The physiologic solution of common salt is made a little less than this strength, 7 to 9 grams per liter (132 gr. to 1 quart), so that when injected by *hypodermoclysis* it will diffuse as freely as blood-serum itself. The laws of osmotic pressure have been a great help to physiologists in solving the problems of secretion and absorption. Cell walls are semipermeable, permitting the cells to lose or gain water according as they are immersed in hypertonic or hypotonic fluids. The red blood-corpuscle keeps its form and semifluid contents while floating in the isotonic serum. Removed to water, it swells to a pale sphere because its envelope is permeable to water, but not to the cell substance which remains within until the corpuscle bursts.

NITROGEN AND THE ARGON GROUP

NITROGEN (Azote)

Symbol, *N*. Atomic weight, 14.01.

Occurrence.—Free nitrogen constitutes four-fifths of the volume of the air, which also contains a trace of it combined, as ammonia (NH_3). It is found in combination in nitrates and many animal and vegetable substances.

Preparation.—To obtain nitrogen from the air, the oxygen must be removed. A piece of phosphorus as large as a pea is floated on a cork in a basin of water, ignited, and covered with a bell-jar. The phosphorus combines with the oxygen, forming clouds of phosphorus pentoxid which are absorbed by the water. Left in the jar is the nitrogen, containing a trace of CO_2 and of argon. Nitrogen can be obtained more pure by not igniting the phosphorus, but by allowing it to oxidize slowly. It can also be prepared by heating a strong solution of ammonium nitrite or a mixture of ammonium chlorid and potassium nitrite.

Properties.—Nitrogen is a colorless, tasteless, inodorous gas, with a specific gravity 0.9701. At $-130°$ C. ($-202°$ F.), under 280 atmospheres, it is condensed into a colorless liquid. It will not support combustion, nor will it burn. It is not poisonous, for if so the air would kill. All animals die in the pure gas, owing to the absence of the life-sustaining oxygen.

Nitrogen Cycle.—Combined with carbon, hydrogen, and oxygen, nitrogen is found in all living things as a constituent of their protein. Abundant as is the free nitrogen of the air, animals and the higher plant forms can not use it directly. It is made available through union with its associate oxygen only by the expenditure of much energy, which is stored up for later work on the decomposition of the resulting compound. Flashes of lightning in nature and powerful electric discharges in a suitable apparatus compel this union. The living energy in the nitrifying bacteria at the roots of pod-bearing plants causes a combination of the two in the nitrates of the soil, which give it fertility. For the growth of crops dependence is largely placed upon animal manures, in the ammoniacal components of which is *combined nitrogen* oxidized by the soil-bacteria to plant-food nitrates. Having been assimilated by the plant, the combined nitrogen is taken up by the animal in the proteins of food, the nitrogen circulating through both in various forms, but always in some compound essential to life. After serving the plant and later the herbivorous animal, the waste nitrogen passes to the soil as a constituent of ammonia, urea, and other excretory products. Again, oxidized by the nitrifying bacteria found in well-aërated soil, it is ready for plant

assimilation as before. Nitrogen forms compounds very slowly, and most of them decompose with great readiness, some of them explosively, giving back the energy taken up in causing their union; namely, gunpowder, nitroglycerin, nitrocellulose, or gun-cotton. Nitrogen imparts an energetic quality to prussic acid, HCN; to nitric acid, HNO_3; to ammonia, NH_3; to powerful alkaloids, and the albuminous principles. These compounds of nitrogen are considered in other places.

Argon and the Noble Gases.—Until recently the inert constituent of the air was considered to be nitrogen only. About 1 part of the 80 per cent. of so-called nitrogen in the air has been proved to consist of argon and its congeners, distinguished by the fact that they show no evidence of chemical attraction, forming no compounds, and hence sometimes called the "noble gases."

Argon (A = 40) was first discovered in 1894 by removing from a measured portion of air first its oxygen, by means of phosphorus or heated copper, and then its nitrogen, by means of red-hot magnesium, by which N is absorbed. By weight it forms 1.2 per cent. of the air, which ratio is constant.

Properties.—Argon is a colorless, odorless, and tasteless gas having a vapor density 19.941. It is soluble in the proportion of 4 parts to 100 of water, and it solidifies under cold and pressure. It has a peculiar spectrum. The chemical inactivity makes it a difficult matter to determine its combining weight, but by physical analogies the conclusion has been reached that it is 40.

Helium (He = 4).—This is a very light gas, with the properties of argon. It was first suspected to be an unknown element of the sun's atmosphere, causing a strong line in the yellow-green of the solar spectrum. The same line has been found, and also those due to argon in the gases evolved on ignition of certain minerals. By cooling these gases to extremely low temperatures they are condensed to a liquid. If the temperature be permitted to rise, the helium becomes a gas first, leaving the argon a liquid. In air, by its evaporation from the liquid state, helium and three other gases with characteristic spectra and different densities have been discovered in amounts as follows: *helium*, 1 in 1,000,000; *neon* (Ne = 20), 1 in 100,000; *krypton* (Kr = 82), 1 in 1,000,000; and *xenon* (X = 128), 1 in 20,000,000.

Niton (Nt = 222.4).—The luminous gas, emanating from radium, has received this name. It is an evanescent element, one-half of it spontaneously changing to radium A and helium in less than four days (p. 248).

CARBON AND ITS OXIDS

CARBON

Symbol, *C*. Atomic weight, 12.

Occurrence.—Free carbon exists in nature in three allotropic forms: as uncrystalline or *amorphous* carbon; *graphite*, either amorphous or imperfectly crystalline; and as *diamond*, in octahedral crystals. In the air it exists in combination as *carbon dioxid.* It occurs widely distributed in the mineral kingdom in *carbonates*, and it is a constituent of all organic substances, being more necessary to the vital processes than any other element.

Properties.—All forms of carbon have the following properties in common: They are solid, tasteless, odorless, and except at very high temperatures, insoluble, infusible, and non-volatile.

Diamond is almost pure carbon; usually being transparent and colorless, though colored specimens are not rare. Particles of carbon in molten iron change to small crystals of diamond by the heat and the pressure of the metal as it contracts on cooling. It is cut into many facets at certain angles, so as to enhance the luster due to its high dispersive and refractive power. As the hardest substance known, it is cut only by its own dust. It has a specific gravity 3.55. It is a non-conductor of electricity and a poor conductor of heat. Resisting all lower temperatures, under the heat of the electric arc, in a vacuum, it is converted into graphite; in the air it burns to carbon dioxid.

Graphite or **plumbago** is a bluish-black, friable substance with a metallic luster, but having a greasy feeling and leaving a line when drawn across paper, hence called *black lead.* It is the "lead" in the common lead-pencil. Its specific gravity is 2.18; its crystals are six-sided plates. The charcoal filaments of the Edison electric lamp in time change by heat to graphite. A good conductor of heat and electricity, it burns at a high heat to carbon dioxid.

Amorphous Carbon.—The purest is *lamp-black*, the soot of burning resins or oils. Other forms less pure are *wood charcoal*, *animal charcoal*, *mineral coal*, and *coke.* All of these are endowed with great energy, convertible into heat, light, electricity, or mechanical motion. When burned in air the end-product is carbon dioxid.

Anthracite and **bituminous coal** are of vegetable origin. The plants of the carboniferous period of geologic history were transformed into coal by decay, heat, and pressure. *Coke* is the charcoal of bituminous coal. *Gas carbon* is a form of coke found in gas retorts and molded to make electric battery carbons and arc lights.

Wood charcoal is used in medicine under the official name *carbo ligni.* Charred bone, or *bone-black*, called *carbo animalis*, contains the mineral ash as an impurity. When washed with hydrochloric acid the ash is dissolved out and there is left *carbo animalis purificatus*, U. S. P.

Uses.—In therapeutics charcoal is valued because it has the power of *adsorbing* foul gases and active oxygen in large volumes. Water having an odor is made sweet, and coloring-matters are removed from various liquids by filtration through charcoal. Applied as a poultice to foul ulcers it not only deodorizes them, but, from the NH_3 and H_2S, by promoting their oxidation, forms acids which destroy and hasten the removal of sloughs.

In the chemical laboratory charcoal is used as a *reducing agent.* Heated to redness it not only takes oxygen from the air to form carbon oxids, but also from metallic oxids, reducing the latter to the metallic state. For this property of extracting metals it is heated with ores in furnaces.

Compounds.—Carbon unites with oxygen, hydrogen, nitrogen, and sulphur to form the very large number of compounds considered in the section of this work entitled Organic Chemistry. Only two of its compounds are considered in this place, the monoxid and the dioxid.

CARBON MONOXID (Carbonic Oxid)

Formula, CO. Molecular weight, 28.

Preparation.—(1) Carbon monoxid (CO) is prepared by passing CO_2 over red-hot coals: $CO_2 + C = 2CO$. (2) By injecting steam into red-hot coals, making *water-gas:* $C + H_2O = CO + H_2$. (3) By burning carbon in an insufficient supply of air. (4) By heating oxalic acid with sulphuric acid,

$$\underset{\text{Oxalic acid.}}{C_2H_2O_4} = \underset{\text{Carbon monoxid.}}{CO} + \underset{\text{Carbon dioxid.}}{CO_2} + H_2O,$$

the mixed gases being deprived of CO_2 by passing through sodium hydroxid.

Properties.—Carbon monoxid is a colorless, tasteless, inodorous gas with a specific gravity 0.967. It is almost insoluble in water and alcohol, but absorbed by ammoniacal solutions of cuprous chlorid, from which it may be reseparated by heat. It burns to CO_2 with a blue flame. This flame is seen burning on the surface of a hard-coal fire, which has at the grate an insufficient supply of air for complete combustion, and hence burns first to CO and later at the surface to CO_2. Likewise, gasoline engines produce it.

Toxicology.—Carbon monoxid often figures in cases of accidental poisoning, as it is the most poisonous constituent in the deadly gas used in cities for illuminating purposes (which may con-

tain as much as 25 per cent.); in that escaping into houses from the defective flues and open stoves; and in "white damp" of mines and furnaces. In the 2000 cases occurring in New York City in 1912, 288 were fatal. The fatal effects are due to the power of CO to enter the blood by the lungs and to form with the coloring matter a close compound, thus destroying the function of carrying oxygen to the tissues. This function depends upon the reversible dissociation of oxyhemoglobin.

$$HbO \leftrightarrows Hb + O.$$

The compound with carbon monoxid, HbCO, is only very feebly dissociable. This property imparts an exceedingly poisonous character to an atmosphere containing more than 0.1 per cent.; when as

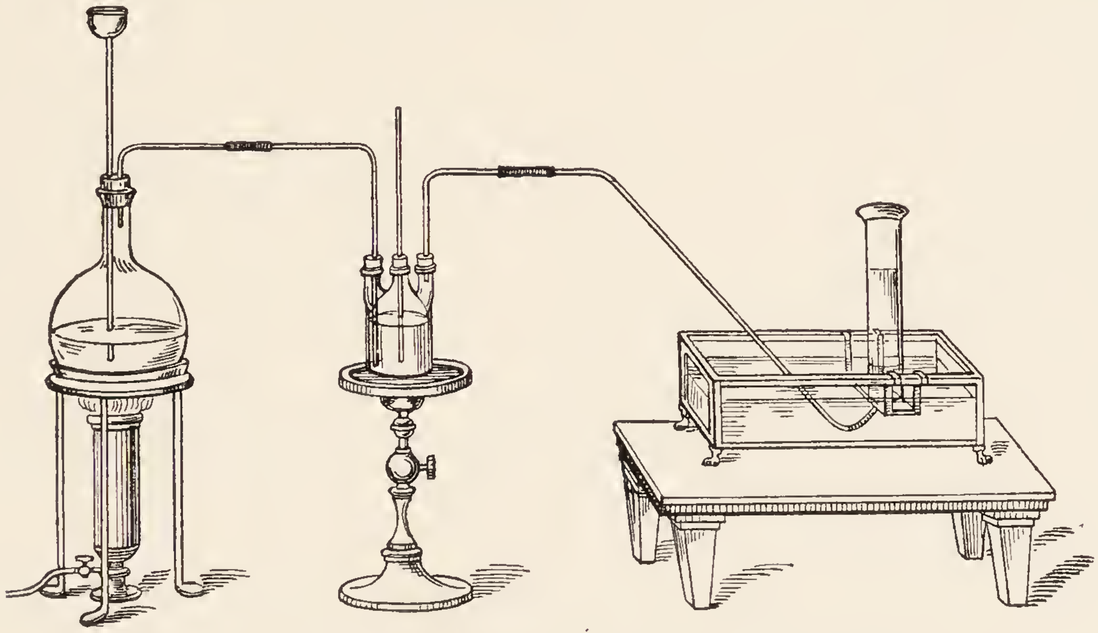


FIG. 35.—Carbon monoxid generated and washed in sodium hydroxid.

much as 0.5 per cent. is present birds are killed in three minutes. The symptoms produced are dizziness, headache, nausea, weakness, retarded breathing, tremor, convulsions, and coma. If a great part of the hemoglobin be saturated with it, death occurs promptly; if there be left unchanged enough to support life, the symptoms are still very grave and the recovery slow, debility and mental dulness persisting for days. It is advisable to practise artificial respiration and inhalation of oxygen, venesection with hypodermic injections or rectal perfusions of *normal salt solution*.[1] The altered blood must be renewed; stimulants, rest, and generous food are the main reliance.

Detection after Death.—In a case of suspected poisoning a portion of the blood is studied by the spectroscope. If the patient lives the poison is usually eliminated within a few hours, but cases are reported of its detection in the blood five and seven days after exposure to the gas. If carbon monoxid be present, the blood will be of a per-

[1] *Normal* or *physiologic salt solution* is usually made of the strength of 0.7 to 0.9 per cent. of common salt, or 60 gr. to the pint of warm water, previously boiled, so as to sterilize it. One pint or quart is injected every hour, as required, beneath the skin of the buttocks or abdomen.

sistently bright-red color, and the spectrum will show a double absorption band, resembling the double band of diluted oxyhemoglobin, but differing in that it is nearer the violet end (Pl. 4, Fig. 1, e). It differs further in not being reduced to the darker color of a single band, even when treated by an ammoniacal solution of ferrous tartrate. When treated on a white plate with sodium hydrate, specific gravity 1.3, the poisoned blood forms a clotted mass, thin layers of which appear bright red, while normal blood turns to a dark slime which in thin layers is greenish brown (p. 538).

CARBON DIOXID (Carbonic Acid Gas, Carbonic Anhydrid)

Formula, CO_2. Molecular weight, 44.

Occurrence.—Free carbon dioxid occurs in nature: (1) Dissolved in the ground-water, and in large proportion a constituent of the ground-air, escaping from volcanoes, accumulating in caves, wells, mines, or any excavation. (2) As a product of putrefaction and of alcoholic fermentation it is abundant in the air of brewer's vats. (3) It is present in the expired air of animals; that exhaled from human lungs contains over 4 per cent. of CO_2, while fresh air contains only 0.04 per cent. (4) In the combustion of wood, coal, or any organic substance the carbon is oxidized to form CO_2. A burner of illuminating gas consumes nearly ten times as much air as a man, and produces six times as much carbon dioxid.

Preparation.—Carbon dioxid can be obtained by the action of any non-volatile acid on any carbonate; but the most convenient source is white marble, a crystalline calcium carbonate, from which CO_2 is evolved by the action of hydrochloric acid.

$$\underset{\text{Calcium carbonate.}}{CaCO_3} + 2HCl = \underset{\text{Calcium chlorid.}}{CaCl_2} + H_2O + CO_2.$$

The apparatus used is the same as that for the preparation of hydrogen (Fig. 28). As one volume of water dissolves an equal volume of the gas it is wasteful to use the pneumatic trough. Being one-half heavier than air, it is easily collected by downward displacement.

Properties.—Carbon dioxid is a colorless, suffocating gas with a slightly acid taste and smell, having a specific gravity of 1.529. Under a pressure of 50 atmospheres at 15.5° C. (60° F.) it is condensed to a transparent liquid. This evaporates so rapidly when liberated that −85° F. is reached and a portion freezes to a snow-like solid. Applied to warts, moles, and superficial tumors, this snow freezes and destroys in thirty seconds. The gas will not burn, nor will it support combustion, but heated to 1300° C. (2370° F.) it breaks up into CO and O. One form of chemical fire extinguisher is an apparatus

for generating CO_2 under pressure, from which the gas is discharged in enormous volumes. Under the names of "black-damp" and "choke-damp" it is an exhalation in mines, dreaded for its suffocative effects. Sometimes there flows from the seams of coal a *natural gas* known as "fire-damp," containing methane CH_4, ethane C_2H_6, and hydrogen. In the pits of the mines it makes with air an explosive mixture. To prevent the accumulation of these gases ventilators are kept going constantly so as to displace them with air. If this is not done a lighted candle or match ignites the mixture with deadly violence, producing carbon dioxid or the "after-damp."

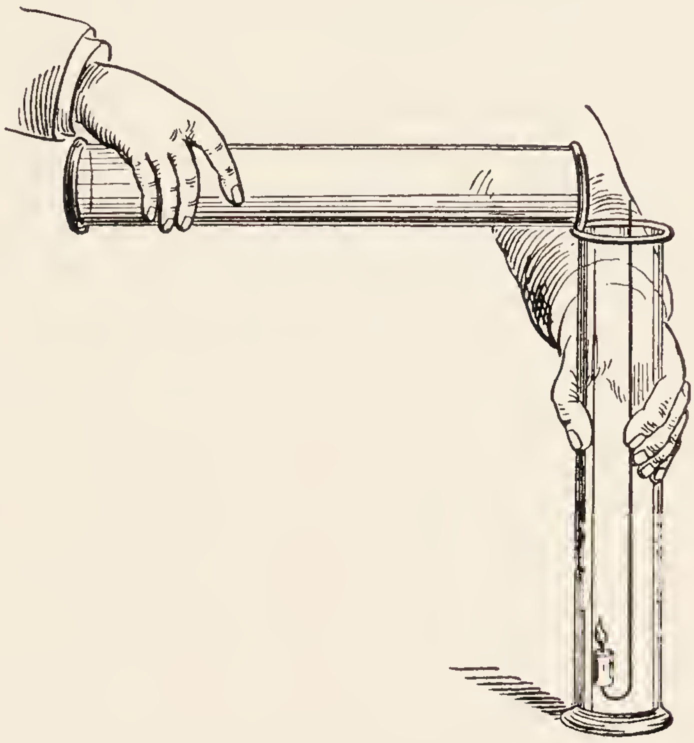


FIG. 36.—Pouring CO_2 downward.

Davy's *safety-lamp* has a chimney of wire gauze through which the flame cannot pass to ignite the explosive gases of the mine. The metal of the gauze cools the flame below the point of ignition.

Aqua acidi carbonici, or *soda water*, is a solution of CO_2 in water under a pressure of 5 atmospheres. At ordinary pressure water dissolves an equal volume of gas and takes up this amount more for each addition of one atmospheric pressure. On opening the bottle the excess escapes as 4 volumes of gas (Carbonic Acid, p. 191).

Detection.—Carbon dioxid extinguishes a flame and forms a white precipitate of carbonates when passed through the hydroxids of calcium or barium.

$$\underset{\text{Calcium hydroxid.}}{Ca(OH)_2} + CO_2 = \underset{\text{Calcium carbonate.}}{CaCO_3} + H_2O.$$

In a mixture of different gases, subjected to the absorbing powers of potassium hydroxid, a lessening of volume denotes CO_2, and the amount of loss is a measure of the quantity of that gas. By aspirating a measured amount of any air through a weighted absorption tube containing potassium hydroxid, the amount of CO_2 is shown by the increase of weight.

The test fluid used by Fitz is dilute calcium hydroxid colored pink by phenolphthalein. Measured quantities of air are agitated with this fluid until it is decolorized. A table gives the CO_2 in parts per 10,000 of the air used.

Tests for Carbonates.—(1) Carbonates treated with hydro-

chloric acid evolve CO_2 with effervescence; the CO_2 passed into lime-water produces a milky precipitate, $CaCO_3$.

(2) In neutral solutions of carbonates, barium chlorid causes a white precipitate of barium carbonate, which dissolves in acids with effervescence.

Constant Proportion of CO_2 in the Atmosphere.—A full-grown man breathes every day about 10,000 liters of air, of which he absorbs about 500 liters of oxygen and exhales about 450 liters of carbon dioxid. Every breath contains enough CO_2 to make a milky precipitate when expired through lime-water. The average amount of CO_2 present in the open air of the country is 0.04 per cent., or 4 parts in 10,000. Notwithstanding the enormous quantities poured into the air from volcanoes, fermentations, respiration of animals, and combustion, the percentage of CO_2 is constant. There is a *state of equilibrium* in which the air continuously loses as much CO_2 as it receives. Some of the carbon dioxid is dissolved by the surface waters of the earth and fixed by the animal organisms—corals, shell-fish, etc., whose skeletons and shells make deposits of earthy carbonates. The greater part, however, is removed by plants which absorb CO_2 through their leaves and roots. In the leaf are cells like the leukocytes of the blood of animals. They contain green granules of chlorophyll which are energized by sunlight, but which are inactive in the dark. The leaf serves as a laboratory in which the chemical powers of the sunlight decompose the CO_2, the plants retaining the carbon and exhaling oxygen in volumes equal to the absorbed gas. This restoration of oxygen compensates for the amount of that gas consumed in the various processes that produce CO_2.

Circulation of Carbon.—The life of organisms is sustained by the transformation of energy, most of which is the energy obtained by the oxidation of carbon. Plants lead a double life. They live and grow by oxidizing the food the sun forms by day in the leaf when they exhale oxygen. In the night when food-making ceases, but growth continues, they exhale, like an animal, a perceptible amount of CO_2. Only by oxidizing the carbon compounds built up by plants, such as sugar, starch, oil, and gluten, can animals support their vital activities. The radiant energy expended by the sun is stored up by plants in amounts sufficient not only for self-maintenance, but also for the supply of energy to repair the waste occasioned by the life-process of all other organisms. The herbivorous animals consume carbonaceous food derived from plants, the carnivora in turn get their energy by feeding upon like material stored in the flesh of the plant eaters.

In the oxidation product, CO_2 of the expired breath, animals return to the air the carbon which it had lost. The CO_2 is carried from the animal tissues to the lungs in combination mainly with

sodium bicarbonate. In the lungs the bicarbonate breaks up, yielding the carbonates again and giving CO_2 and H_2O to the expired breath, thus reversing the reaction.

$$\underset{\text{Sodium bicarbonate.}}{2NaHCO_3} \rightleftarrows \underset{\text{Sodium carbonate.}}{Na_2CO_3} + CO_2 + H_2O.$$

Each of the two living kingdoms of nature supports the other in an eternal circuit of energy, obtained originally in kinetic form from the sun's rays and carried potentially by the carbon, on the one hand, and the oxygen, on the other. The production of wood (cellulose) and the energy used is in the sense of the equation:

$$6CO_2 + 5H_2O + 671{,}000 \text{ calories} \rightleftarrows C_6H_{10}O_5 + 6O_2.$$

A part of the carbon of plants which does not soon return to the air is preserved in the storehouse of the soil as combustible substance. A peat deposited in bogs or in the fossilized form of coal, the carbon reappears in aftertimes to heat the boiler of the steam engine, and thus becomes the most abundant store of energy used in the mechanic arts.

The average composition of air may be said to be in 100 vols.:

	When inspired.	When expired.
Oxygen	20.60 vols.	16 vols.
Nitrogen	76.90 "	77 "
Argon	1.00 "	1 "
Carbon dioxid	0.04 "	4 "
Aqueous vapor (about)	1.46 "	2 "
Ammonia	traces.	
Ozone	traces.	
Nitric acid	traces.	
Marsh gas	traces.	
Sulphurous anhydrid	traces.	
Sulphuretted hydrogen (in towns)	traces.	

In the proportion of argon given above is included its congeners, helium, neon, crypton, and xenon.

Excess of CO_2 in Air.—When the circulation and diffusion of the air is interfered with by confinement in caves, wells, mines, vats, or badly ventilated rooms, it accumulates CO_2, and when the proportion reaches 0.7 per cent. it is said to be *contaminated.* If the CO_2 be derived from respiration or combustion the air at the same time loses oxygen, so that an increase of CO_2 from these sources is most serious in its influence upon health.

The **cubic space for dormitories** allowed each person should be, for the healthy, at least 400 cu. ft.; for the sick, occupying the same room day and night, 850 cu. ft.; for lying-in cases and those having offensive diseases, 1200 cu. ft. To calculate the largest number of persons that ought to sleep in a room, measure the length, breadth, and height of the room and multiply them to get the cubic contents. Divide the cubic contents by 400 and the quotient is the number of healthy occupants, which should

not be exceeded if we would avoid contamination of the air from overcrowding.

Poisonous Effects.—Pure carbon dioxid causes instant suffocation by spasm of the glottis. When the CO_2 is simply added to the air, as in the industry of making soda-water, or as in the discharge into free air from carbonated springs and other natural sources, an addition of 10 to 15 per cent. will render the air poisonous, but not immediately fatal. A candle would still burn in this air, though dimly, but when the proportion reaches 16 per cent. the flame is extinguished. It would be fatal to go into any confined space where a candle will not burn. When the contamination of confined air is due to respiration or combustion, and the reduction of oxygen corresponds to the increase of CO_2, we feel oppressed by 0.1 per cent., and instinctively escape from it. Greater discomfort is produced by 1 per cent.; headache, dizziness, and nausea may be caused by 2 per cent.; an atmosphere containing 3 per cent. does not kill, though it causes profound disturbance of health, but 5 per cent. may be fatal from asphyxia.

Treatment.—The indication is to get into the lungs a large amount of pure air or oxygen as quickly as possible.[1] To do this, the patient must be instantly removed to fresh air, and artificial respiration practised with inhalations of oxygen. Respiration is stimulated by rhythmic pressure on the chest, traction of the tongue, slapping with a wet towel, galvanism, and friction of the extremities. These measures must be kept up for an hour, if necessary. When breathing is established, warm applications should be made to the extremities, and the body well wrapped in woolens, while coffee or brandy is administered internally.

The Atmosphere.—The proportionate mixture in the atmosphere has been stated above. The 20.6 per cent. of oxygen supports animal life; the 76.9 per cent. of nitrogen serves to dilute the oxygen; the 0.04 per cent. of CO_2 and the trace of ammonia nourish plants; water, to the extent of 1.46 per cent., favors the absorption of these foods and ozone purifies the air.

Physical Properties.—A liter of air weighs 1.293 gm. Having covered an open receiver with the hand and removed the air with an air-pump, the pressure of the atmosphere is felt as a force of 15 lbs. on every square inch (1033.3 gm. on every square centimeter). The whole body must support the pressure of several tons, and that it is able to do so is due to the fact that the pressure

[1] It often happens that the patient is first seen lying unconscious at the bottom of a well or pit or vat. Rescue seems impossible because others descending are instantly suffocated. In such cases great success has followed the following procedure: A condenser of oxygen, holding 240 gallons of the gas compressed in a cylinder, is obtained from a hospital or a theater using oxygen for the oxycalcium light. Through a hose reaching to the bottom of the pit the gas is discharged not only to revivify the patient, but to displace the CO_2, so that others can descend to his assistance.

is exerted equally in all directions, thus canceling the pressure on any one point.

The variations of atmospheric pressure from day to day, or at different heights, are measured by the *barometer*. In its simplest form this instrument is a strong, straight glass tube, about 33 in. (800 mm.) in length, closed at the top. The lower end, which is open, dips into a small cistern of mercury. This tube is first filled with mercury and then inserted in the cistern with the open end under the liquid. The mercury of the tube falls to a point about 30 in. (760 mm.) from the level of the cistern. The unoccupied space above the mercury is a vacuum. The pressure of the air outside upholds the column inside. As the air grows heavier the pressure forces the mercury higher; as the air declines in pressure, the mercury falls. In ascending a mountain the column of air above is reduced in height, and, therefore, the barometric column falls 1 in. for every 900 ft. of elevation.

Gases are highly compressible, shrinking in volume regularly as the pressure increases (Boyle's law). On the other hand, the volume increases regularly with equal additions of absolute temperature (Charles' law). To compare the volumes of gases observed at different times, it is necessary that the pressure of the air and the temperatures at the times of observation be alike. As this is practically impossible from day to day, or hour to hour, it has been agreed to reduce the observed volumes of gases to standard conditions. By means of a formula the observation is converted to the standard barometric pressure of 760 mm., and at the standard temperature of 0° C.

$$V' = \frac{V(b - w)}{760(1 + 0.00366\ T)}.$$

In this formula: V' = volume required; V = the volume observed; b = barometer in mm.; w = tension of aqueous vapor (table, p. 40); T = observed temp. Centigrade (p. 30, footnote).

Recent studies on the expansion of very dilute gases show that at a certain stage of dilution the ability to expand is much lessened. This justifies the inference that the air does not extend indefinitely into space, becoming progressively more attenuated, but that at a distance of two hundred miles, more or less, it has a definite limit.

When air is compressed 2000 pounds on the square inch, cooled with cold water, and then permitted to expand, it makes a low temperature for cooling another portion of compressed air. This in expanding cools another portion to a much lower temperature and, repeating this cycle of operations for the third time, the compressed air in expanding through a small opening is cooled below its *critical point* and liquefies.

Liquid air can be obtained in any quantity by the expenditure of power. It is a bluish mobile liquid boiling at $-190°$ C. ($-376°$ F.), and is used for procuring that temperature for experimental purposes. Immersed in it mercury freezes so hard that a piece can be used to hammer a nail; rubber and meat become as brittle as thin glass, alcohol solidifies like ice. Many forms of bacteria survive this exposure with only a temporary suspension of vitality, and seeds of grain and peas after hours of immersion showed subsequent power of germination. As the air boils, the first more volatile portion extinguishes a flame; it is nitrogen. After a time the boiling vapor starts a glowing ember into flame, and we find that the liquid left is nearly pure oxygen, which has a higher boiling-point than the nitrogen.

CHEMICAL PHILOSOPHY

In another place (p. 70) illustrations have been given of Lavoisier's law, that of Definite Proportions: *i. e., A definite compound always contains the same elements, united in the same proportions.*

There are five compounds of nitrogen and oxygen. The formulas, names, and compositions by weight are as follows:

	N.	O.	
N_2O	28	16	Nitrous oxid.
NO	14	16	Nitric oxid.
N_2O_3	28	48	Nitrogen trioxid or Nitrous anhydrid.
N_2O_4	28	64	Nitrogen tetroxid or Nitrogen peroxid.
N_2O_5	28	80	Nitrogen pentoxid or Nitric anhydrid.

These compounds are illustrations of Dalton's second law, that of Multiple Proportions: *When two bodies, simple or compound, unite in several proportions, the weight of one being constant, the weights of the other vary according to a simple ratio.* When composed of two elements they are said to be *binary.* In nomenclature the name of the electropositive element in full is placed first; then follows the name of the electronegative element, with a suffix derived from the Greek numerals and the termination *id.* In an older method the name of the electropositive element was modified by adding *-ic* or *-ous* to the first syllable of the electropositive element. *Nitrous* means less and *nitric* means more of the other or electronegative element. For the other compounds the prefix *hypo-* means less and *per-* means more of the electronegative element.

In union with H_2O, the first, third, and fifth of the above-named form acid *ternary* compounds of three elements, nitrogen with hydrogen and oxygen, as follows:

$H_2N_2O_2$ or HNO	Hyponitrous acid.
$H_2N_2O_4$ or HNO_2	Nitrous acid.
$H_2N_2O_6$ or HNO_3	Nitric acid.

There is another generalized statement of facts, developing logically from the first and second laws—Equivalent Proportions: *The proportions in which two or more bodies unite with another is either the same as that in which they unite with themselves or a simple multiplc of it.*

ATOMIC THEORY

In studying the phenomena of allotropism of oxygen and carbon (see pp. 74 and 99) the conclusion becomes inevitable that nature, as we know it, behaves as if it were composed of minute separate particles, variously grouped in different bodies and in allotropic forms of the same substance. This conception came early in the history of thought, the first definite statement of the doctrine of atoms being attributed to Democritus (400 B. C.). As further developed by Lucretius, it may be summarized as follows: The bodies which we see and handle, which we can break in pieces and destroy, are composed of smaller bodies which we cannot see nor handle, which are always in motion, are centers of energy, and are not broken nor in any way destroyed by us. In the recent century of great chemical and physical discoveries each new fact has found a place in the structure of this theory. All attempts have failed to account for chemical phenomena on the opposed hypothesis of the homogeneous structure of matter. The only consistent view of matter is that it is not uniform and continuous throughout, but grained. The grains are *molecules* (see p. 28) which have still smaller constituents, *atoms*. The atoms are undestroyed by the chemical force which keeps them combined in molecules and which controls their movements and associations. To these properties Dalton, in 1808, proposed that there be added others, to wit: (1) all the atoms of any one element have equal mass or weight; (2) the atoms of different elements have different weights; (3) the atomic weights be related as are the combining weights.

As it is not divided in chemical reactions, the atom is the smallest quantity of an element that can enter into chemical combination.[1] When two elements combine, one atom of one

[1] Recent study of radio-active metals (p. 250) has established certain facts of wide range that do not fit into the atomic theory unless the intellectual conception of the atom be elaborated. The new conception symbolizes the new facts by giving a mechanical interior structure to the atom. It is conceived that in the sphere of the atom are a number of gyrating corpuscles (*electrons* with a mass one 1700th that of the hydrogen atom), acting as a unit because in a state of equilibrium which resists the separating power of chemical operations and hence just so far justifies the assumption that atoms are indivisible. The atom-complexes of the radio-active elements, however, are in a state of unstable equilibrium, exhibiting energy in the form of heat, light, etc., while the atom-complex as a whole, losing some electrons, changes in properties as it declines in mass to stable forms which are permanent.

element is placed in juxtaposition with one or more atoms of the other. It follows that the weights of two elements uniting will be in the same proportion as the constant weights of their atoms. This is the explanation of the law of definite or constant proportions. Thus, if the relative weights of atoms of sodium and chlorin are as 23 to 35, and combination is simply juxtaposition, then sodium chlorid can contain its elements only in the proportion of 23 parts of sodium to 35 of chlorin.

Again, if one element, C, forms two compounds with another element, O, the first one of which contains one atom of C and one atom of O and the second contains one atom of C and two of O, it is plain that the masses of O which unite with the fixed mass of C must be in a ratio by a whole number. Thus, 12 weights of C unite with 16 of O to make CO. But as O forms another compound to the constant weight 12 of C, it can not have less than 16 of O, for that would be to split an atom, which is postulated to be impossible. The mass of O must be either the first weight, 16, or some simple multiple, such as 1 : 2, so it takes 32 of O and forms OCO or CO_2. By almost universal consent chemists refer all the facts of their science to the one general law above stated—that is, that elements are composed of atoms having the same weights for the same kind, but different weights for different kinds. By means of this law the chemist determines not only the nature and number of the atoms in a molecule, but also their arrangements. In no other way can we account for the compounds called *isomeric*, which show that two or more distinct substances may yet have the same number of the same atoms in the molecule.

As stars in a system are kept in place by gravitation, so in a complex molecule atoms in various groups are held together by chemical attraction. A molecule of common alcohol, also that of methyl-ether, contains one atom of oxygen, two of carbon, and six of hydrogen. There is sound experimental basis for the conclusion that, although they have the same elements in the same proportion, the groups of atoms in methyl-ether are $O\Big\langle\begin{array}{l}CH_3\\CH_3\end{array}$ and of alcohol are $\begin{array}{l}HO.CH_2.\\ \qquad\;\; | \\ \qquad CH_3\end{array}$ Powerful external forces may break up the mutual attraction of large groups, but only to prove that the members of a smaller group have the greatest attraction for one another by the persistence of the original arrangement of their atoms. The atoms of the group CH_3 remain subject to each other's influence through many vicissitudes and varying associations.

The *atomic weight* (A. W.) of an element is the weight of one atom of that element as compared with the weight of an atom of hydrogen. (For "intra-atomic matter," see p. 250.)

The *molecular weight* (M. W.) of a substance is the weight of its molecule, as compared with the weight of an atom of hydrogen.

As all gases are affected equally by temperature and pressure their molecular constitution must be alike. The *law of Avogadro* assumes that *equal volumes of all gases at the same temperature and pressure contain an equal number of molecules.* It follows from this law that the molecular weights of gases are proportional to the weights of equal volumes—that is, to their specific gravities. The molecular weight is the sum of the atomic weights; hence if hydrogen be the unit, its molecular weight is 2, there being 2 atoms in its molecule. To obtain the molecular weight of another gas, all that is necessary is to double its density. The vapor density is the specific gravity with hydrogen = 1. M. W. = 2 × V. D. (H = 1). Expressed in terms of ordinary specific gravity (air = 1), we must allow for the fact that air is 14.43 times heavier than hydrogen; then the molecular weight of a gas equals the specific gravity multiplied by 14.43 and by 2; or M. W. = 28.86 × S. G. (air = 1). Thus: the density of ozone (H = 1) is approximately 24, which when doubled becomes 48. The weight of each atom being 16, which is one-third of 48, there must be three atoms in its molecules and its formula must be O_3.

From what has been said above it might be expected that in chemical combinations of elementary gases the *volumes entering into the union would hold some simple relation to each other.* In fact this is *Gay-Lussac's law.* Moreover, *the product of the reaction* (the compound gas) *has the volume of a simple multiple, usually* 2, *even when the original single volumes were* 3 *or* 4. For example: when united,

1 vol. of	hydrogen	+ 1	vol. of	chlorin	yield	2	vols. of	HCl.
2 vols.	"	+ 1	"	sulphur	"	2	"	H_2S.
2 "	"	+ 1	"	oxygen	"	2	"	steam.
3 "	"	+ 1	"	nitrogen	"	2	"	NH_3.

Summary.—A *molecule* is the smallest particle of a substance that exists free and stable.

An *atom* is the smallest characteristic part of an element that is combined in the molecule by chemical action.

A *compound* is composed of molecules which contain two or more different kinds of atoms united.

An *element* is composed of molecules which contain but one kind of atom.

An *electron* is the negatively electrified particle contained in all atoms, and of which there are at least 1700 in a hydrogen atom.

Chemical union is due to electric attractions; electronegative ions have a few more electrons than exactly balance their positive electricity; electropositive ions have a few less. When they meet they unite in a neutralized molecule (pp. 46 and 50).

Law of combination by volume. *Gaseous elements combine in equal volumes for their respective atomic weights.*—Though HH+OO+HH unite as three equal volumes they shrink to two volumes of water vapor, HOH+HOH.

Symbols and Formulas.—In place of records of composition and lengthy descriptions of reactions it has been found convenient to use a shorthand system of symbols and equations. The symbol of an element is usually the initial letter of its name (English or Latin); when the names of two or more elements have the same initial, a second letter is added in smaller type. This second letter is the next vowel or a prominent consonant. Thus, Boron, Barium, Berryllium, Bismuth, and Bromin have the symbols B, Ba, Be, Bi, and Br, respectively. The choice of the single initial is given to the non-metal—in this case to Boron.

The formula of a compound is made by printing as close as the types permit the symbols of the constituent elements: thus, copper oxid is CuO.

The chemical symbol has a much more complex function than that of an algebraic one, like x and y, which stand for simple quantities. The chemical *symbol* represents, first, the name of an element; second, one atom; third, a constant definite proportion, called the atomic weight; fourth, a single gas volume. Thus, O stands for oxygen, 1 atom, 16 weights, and 1 volume.

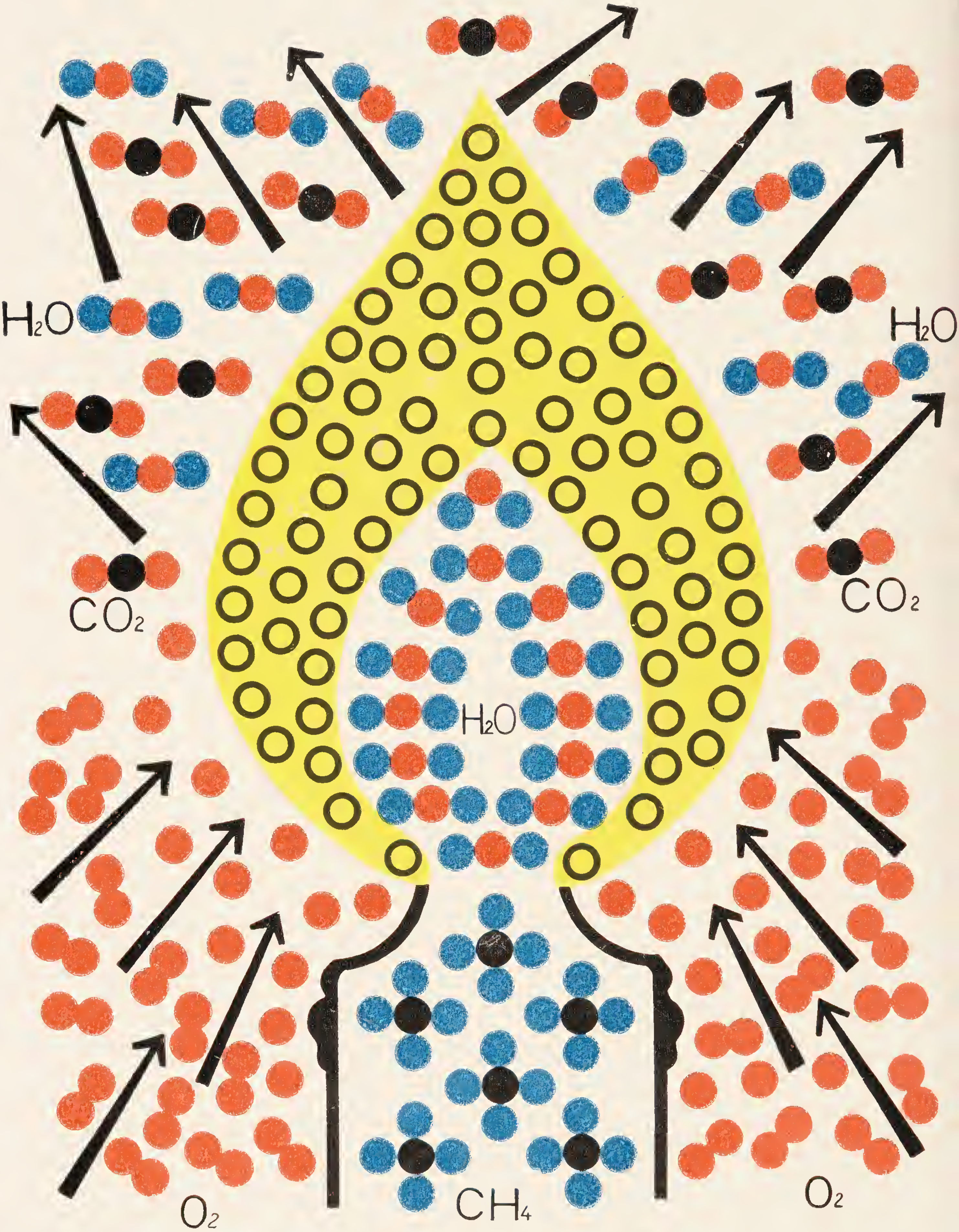
The *formula* of a compound denotes the name of its elements, the atoms in one molecule, the constant molecular weight, and two gas volumes.

Thus, H_2O_2 stands for hydrogen dioxid, 4 atoms in its molecule, a molecular weight of 34 (2 for the H_2 and 32 for the O_2), and 2 gas volumes. It will be observed that when the molecule contains two or more atoms of the same kind the formula shows it by the small coefficient following, placed below the line. Thus, H_2O, CO_2.

If it be desired to express more than one *molecule* of a compound, a large figure is used as a coefficient before the formula; thus, $2HNO_3$ represents not simply 2 atoms of hydrogen, but 2 molecules of nitric acid.

Three different kinds of formulas may be used to represent the same compound. When it is desired to express the composition only, an *empiric* formula is used, which gives in the smallest number the proportions of the atoms. A *molecular* formula is a rational attempt to give the actual number of atoms in the molecule, and this may be a multiple of the empiric formula.

PLATE I.



ATOMIC THEORY OF A HYDROCARBON FLAME.

The red discs are oxygen atoms, the black are carbon, the blue are hydrogen; the black circles in the yellow zone are incandescent carbon atoms emitting light. The products of the combustion are water and carbon dioxid.

When there is experimental ground for assuming that the internal grouping of the atoms is known, the facts are indicated by the arrangement of the symbols of the atoms, thus making the formula *constitutional.* Thus, ferric hydroxid may be denoted by either of the following formulas:

Empiric and molecular . . . . FeH_3O_3.
Constitutional . . . . $Fe(OH)_3$.

Nascent State.—When an element has just been released from combination, it is observed to have more powerful attractions than are shown by it after the first moment of new birth has passed. This transition phase of higher energy has received the name *nascent state.* It is often purposely produced to secure the highest capability of the element for effecting chemical changes. According to the atomic theory, the transient state is one of single atoms energetically drawing others to them. With free affinities they are ready for fresh unions. Finding no dissimilar element to attract, they must at last combine with like companions to make stable molecules of the same elements. The atoms are now without free affinities, tied up in a combination which must be broken afresh before they can form another with atoms of a different element.

The properties ascribed to the chemical atom express its actual relations. With its intra-atomic gyrating electrons it is a conception in the highest degree useful for a working chemist as well as for the physicist. Its diameter is about $\frac{1}{100}$ millionth of a centimeter; the electron is about $\frac{1}{100}$ thousandth that size.

A graphic picture is here shown (Plate 1) of what the chemist imagines to occur when he explains the burning of common illuminating gas in a luminous flame:

$$CH_4 \quad + \quad 2O_2 \quad = \quad CO_2 \quad + \quad 2H_2O.$$

It must be remembered that in this plate nothing is postulated of the atom as to its color or form or relations in space.

Carbon atoms are represented by black discs, which become bright at a high heat; hydrogen atoms are blue; oxygen, red. These colors serve simply to distinguish the elements.

Molecules of CH_4 stream out at the burner, a match heats it to the point required to unite it with oxygen. The free oxygen of the air in molecules, when heated, dissociates into atoms, which at once unite with the hydrogen of CH_4 to form molecules of H_2O. Their union causes heat sufficient to raise the carbon atoms of CH_4 to incandescence, furnishing light as they pass through the hot zone. At the outer margin they meet oxygen atoms heated and combine with them to form CO_2. At the center

is the combustible gas CH_4 yet unburned, surrounded by a cone of incandescent carbon which deposits soot on a cold surface and on the outer edge is the hottest zone due to the final burning of the carbon. If sufficient air be mixed with the gas before ignition, as in a *Bunsen burner*, or if air be blown in by a *blow-pipe*, a more intense heat is obtained all through the flame. The illuminating and soot-making powers then disappear, because the carbon burns at once with the hydrogen and there is no luminous cone of white-hot carbon atoms.

Valence, Atomicity, Quantivalence.—When two substances have acted upon each other and caused transformations, they are said to have *entered into reaction.*[1]

The atomic weights of the elements do not express their relative values in the mutual reactions.

In the equation $Zn + H_2SO_4 = ZnSO_4 + H_2$, 1 atom of zinc proves its equal value to 2 of hydrogen by exchanging for the hydrogen atoms, taking their place. The zinc is accepted by the SO_4 as being equal in chemical power to the 2 hydrogen atoms. In the same way 1 atom of chlorin is substituted for 1 atom of hydrogen; 1 of oxygen for 2 of hydrogen; 1 of nitrogen for 3 of hydrogen; 1 of carbon for 4 of hydrogen; 1 of phosphorus for 5 of hydrogen; and 1 atom of sulphur for as many as 6 atoms of hydrogen. This value of a combining atom compared with that of an atom of hydrogen is called its *valence*, *valency*, or *quantivalence*. If its valence is equal to one of hydrogen, it is *monovalent* or *univalent* and is termed a *monad*, such as Cl, Br, I, K, Na, Ag; one of double value is *divalent* or *bivalent* and is termed a *dyad*, as O, S, Cu, Hg, Zn, Ca; one of triple value is *trivalent* and called a *triad*, as P, As, Sb, Bi; one of quadruple value is *tetravalent* or *quadrivalent*, and is called a *tetrad*, as C, Si, Al, Pt, Pb; one of quintuple value is *pentavalent* or *quinquivalent*, called a *pentad*, as P.; one of sextuple value is *hexavalent* or *sexivalent*, and called a *hexad*, as S.

The cause of valence has not been determined, though a recent speculation concerning it may prove of some help. The work of Faraday embodied in his laws (p. 52) showed that the electric charge of an ion was proportional to its valence. As nearly all chemical action is between charged ions, one charge may stand for univalence, then a bivalent ion is one that carries two charges, the trivalent, three, and so on. The amounts of the different ions carrying the same charge are in the proportion of the atomic weights of the ions. To set free a bivalent ion requires twice as

[1] The word *reaction* is also used to describe the effect of acids and bases on certain colored indicators, such as litmus. The reaction is *neutral* when it does not alter the color of either red or blue litmus; it is *acid* when it turns blue litmus red; *alkaline* when it turns red litmus blue.

much electricity as to free a univalent one and the trivalent thrice and so on. No ion has more than eight charges (octivalent), and none has less than one, which is that of hydrogen. Each valence is sometimes referred to as a *bond* or *link* of attachment. It is sometimes symbolized by radiating strokes and sometimes by accent marks and Roman numerals, placed above and to the right of the symbol of the element, thus:

H –	. . . .	H'
– O –	. . . .	O''
\/ N |	. . . .	N'''
| – C – |	. . . .	C^{IV}
\\\|/ P /\\	. . . .	P^{V}
\/ – S – /\\	. . . .	S^{VI}

Variation of Valence.—The valence of an element is not a fixed and unchanging quantity; thus, nitrogen in nitrous oxid, N_2O, is a monad; in ammonia, NH_3, it is a triad, and in ammonium chlorid, NH_4Cl, it is a pentad.

In view of the fact that the valence of an element may vary with the temperature, with the nature of the other substance, and with unknown conditions, it cannot be considered an absolute endowment of the atom, but only as a statement of its attractive power in the special class of compounds being studied.

Graphic Formulas.—In another place (p. 110) two methods of notation were used for one substance. These were called the empiric and constitutional formulas of ferric hydroxid. In addition to these methods of noting the results of discovery chemists sometimes fix the impression they have received as to the internal arrangement of a complex molecule by a *graphic formula.* When it is desired to show that the iron in ferric hydroxid acts as a trivalent atom, and that the hydroxyl groups are monovalent, the following graphic form is used:

$$\text{Ferric hydroxid} \quad . \ . \quad Fe(OH)_3 \quad . \ . \quad \begin{array}{c} \mathrm{H} \\ | \\ \mathrm{O} \\ | \\ \mathrm{H-O-Fe-O-H.} \end{array}$$

Classification of the Elements.—In an earlier section (p. 65) the elements to be studied were grouped in classes for emphasizing certain important properties. That arrangement, while serving the purpose at that point, does not pretend to be the only one of value. For different needs there are different lists, more or less special or one-sided. The ordinary table is alphabetic, the only claim made for it being that it is easy for reference.

In the *periodic system* Mendelejeff has grouped them by their valence, and the elements thus allied he has placed in the order of their atomic weights, so as to emphasize the significant fact that they differ from each other by approximately a multiple of the number 8. It has been shown that with this regular numeric increase in atomic weights there is a corresponding progression of properties, thereby raising the presumption that *the physical and chemical properties of elements, and also the constitution and properties of their compounds are periodic functions of the atomic weights* (*Mendelejeff's periodic law*).

When the atomic weights were first calculated hydrogen was taken as 1, and oxygen was found to be 16. As nearly all the elements unite with oxygen, their atomic weights were calculated on the basis of $O = 16$, and these weights have been in use many years. It has been discovered, however, that there was a mistake, and that if $O = 16$, then H is not 1, but 1.008. The whole question is simply one of convenience, and as the table based on $O = 16$ is adjudged best by some of the most authoritative chemical societies, it is the one used in the present work. For the purpose of simplifying study in the body of this work, the nearest integer is used, the fractions being ignored.

The table that follows on pp. 117 and 118 is not Mendelejeff's, though it is based upon the periodic system. In perpendicular columns similar elements are grouped in sections by their numeric values.

In the section where the valence is marked 0 will be found the argon family of atmospheric elements, which are unable to unite with other elements. In the next section, marked I., are hydrogen and the alkali metals. In the next, marked II., are the divalent alkaline earth metals and the heavy metals of the zinc family. The section marked III. contains trivalent boron, the earth metals, and the corresponding heavy metals, gallium and indium. Section IV. contains two tetravalent non-metals and metals of the titanium family, along with those of the tin family. Section V. contains elements that are pentavalent or trivalent, such as the nitrogen family. In Section VI. are elements that are divalent or hexavalent. In Section VII. are the halogens, which are univalent or heptavalent, and three metals that are divalent on the one hand

or heptavalent on the other. In the last section are the metals which cannot be placed in any previous class—the iron and the platinum families.

Elements Arranged in Arithmetic Progression according to Atomic Weight and Valence

Name.	Derivation.	Symbol.	Atomic Weight. O = 16	Atomic Weight. H = 1	Valence.
Helium	Gr. *helios*, sun	He	4.00	4.000	0
Neon	Gr., new	Ne	20.00	19.900	0
Argon	Gr., without energy	A	39.90	39.600	0
Krypton	Gr., hidden	Kr	83.00	82.400	0
Xenon	Gr., stranger	X	130.70	129.800	0
Hydrogen	Gr., water-forming	H	1.01	1.000	I.
Lithium	Gr. *lithos*, stone	Li	7.00	6.970	I.
Sodium (*natrium*)	Eng. *soda*	Na	23.00	22.880	I.
Potassium (*kalium*)	Eng. *potash*	K	39.10	38.820	I.
Rubidium	L. *rubidus*, red (its spectrum)	Rb	85.45	84.750	I.
Cesium	L. *cæsius*, sky-blue "	Cs	132.81	131.900	I.
Glucinum (*beryllium*)	Gr. *glykys*, sweet	Gl	9.10	9.000	II.
Magnesium	*Magnesia*, district in Thessaly	Mg	24.32	24.100	II.
Calcium	L. *calx*, lime	Ca	40.09	39.800	II.
Zinc	Ger. *zink*	Zn	65.37	64.900	II.
Strontium	*Strontian*, a town in Scotland	Sr	87.62	86.950	II.
Cadmium	Gr. *cadmeia*, calamine	Cd	112.40	111.550	II.
Barium	Gr. *barys*, heavy	Ba	137.37	136.400	II.
Mercury	Name of planet	Hg	200.00	198.500	I. or II.
Radium		Ra	226.40	224.390	II.
Boron	*Borax*	B	11.00	10.900	III.
Aluminum	L. *alumen*, alum	Al	27.10	26.900	III.
Scandium	*Scandinavia*	Sc	44.10	43.800	III.
Gallium	L. *Gallia*, France	Ga	69.90	69.500	III.
Yttrium	*Ytterby*, a town in Sweden	Yt	89.00	88.300	III.
Indium	From its *indigo* spectrum	In	114.80	113.100	III.
Lanthanum	Gr. *lanthano*, conceal	La	139.00	137,600	III.
Neodymium	Gr. *neo*, new, and *didymos*, twin	Nd	144.30	142.500	III. or IV.
Praseodymium	Gr. *praeseo*, green, and *didymos*	Pr	140.60	138.400	III. or IV.
Samarium	*Samarski*, a Russian savant	Sm	150.40	149.200	III.
Gadolinium	*Gadolin*, a Russian chemist	Gd	157.30	155.800	III.
Terbium	*Ytterby*, a town in Sweden	Tb	159.20	158.800	III.
Erbium	*Ytterby*, a town in Sweden	Er	167.40	164.700	III.
Thulium	*Thule*, Northland	Tu	168.50	169.400	III.
Ytterbium	*Ytterby*, a town in Sweden	Yb	172.00	171.900	III.
Thallium	Gr. *thallos*, budding twig	Tl	204.00	202.610	I. or III.
Carbon	L. *carbo*, charcoal	C	12.00	11.900	IV.
Silicon	L. *silex*, flint	Si	28.30	28.200	II., III. or IV.
Titanium	L. *Titanes*, sons of the earth	Ti	48.10	47.800	IV.
Germanium	L. *Germania*, Germany	Ge	72 50	71.900	II. or IV.
Zirconium	Ar. *zarkun*, gold-colored	Zr	90.60	69.700	IV.
Tin (*stannum*)	Anglo-Saxon	Sn	119.90	118.100	II. or IV.
Cerium	Planet *Ceres*	Ce	140.25	138.000	III. or IV.
Lead (*plumbum*)	Anglo-Saxon	Pb	207.10	205.360	II. or IV.
Thorium	God *Thor*	Th	232.42	230.800	III. or IV.
Nitrogen	Gr., niter-forming	N	14.01	13.930	III. or V.
Phosphorus	Gr., light-bearing	P	31.00	30.750	III. or V.
Vanadium	Goddess *Vanadis* (Freya)	V	51.20	51.000	II., III. or IV.
Arsenic	L. *arsenicum*	As	74.96	74.350	III. or V.
Columbium (*niobium*)	*Columbia*	Cb	93.50	93.000	III. or V.
Antimony (*stibium*)	L. *antimonium*	Sb	120.02	119.500	III. or V.
Tantalum	*Tantalus* (Gr. myth.)	Ta	181.00	180.000	V.
Bismuth	Ger. (unknown origin)	Bi	208.00	206.500	III. or V.

Elements Arranged in Arithmetic Progression according to Atomic Weight and Valence—Continued

Name.	Derivation.	Symbol.	Atomic Weight. O = 16	Atomic Weight. H = 1	Valence.
Oxygen	Gr., acid-forming	O	16.00	15 880	II. or VI.
Sulfur (Sulphur)	L. *sulphur*	S	32.07	31.830	II. or VI.
Chromium	Gr. *chroma*, color	Cr	52.00	51.700	II. or III.
Selenium	Gr. *selene*, moon	Se	79.20	78.600	II. or VI.
Molybdenum	Gr. *molybdos*, lead	Mo	96.00	95.300	II., III., IV. or V.
Tellurium	L. *tellus*, earth	Te	127.50	126.500	II. or VI.
Tungsten (*wolframium*)	Swed., heavy stone	W	184.00	182.600	II., IV., V. or VI.
Uranium	Planet *Uranus*	U	238.50	237.800	III., IV., V., VIII.
Fluorin	L. *fluor*, < *fluo*, flow	F	19.00	18.900	I. or VII.
Chlorin	Gr. *chloros*, green	Cl	35.46	35.180	I. or VII.
Manganese	L. *magnes*, magnet	Mn	54.93	54.600	II., III. or IV.
Bromin	Gr. *bromos*, stench	Br	79.92	79.340	I. or VII.
Ruthenium	Rus. *Ruthenia*	Ru	101.07	100.900	II., III. or IV.
Iodin	Gr. *iodes*, violet	I	126.92	125.890	I. or VII.
Osmium	Gr. *osme*, odor	Os	190.90	189.600	II. or IV.
Iron (*ferrum*)	Anglo-Saxon, *iren*	Fe	55 85	55.860	II. or III.
Nickel	Ger. *kupfernickel*	Ni	58.68	58.250	II. or III.
Cobalt	Ger. *kobold*, goblin	Co	58.97	58.550	II. or III.
Copper	L. *Cyprus*	Cu	63.57	63.100	I. or II.
Rhodium	Gr. *rhodon*, rose	Rh	102.90	102.200	III.
Palladium	Planet *Pallas*	Pd	106.70	106,200	II. or IV.
Silver (*argentum*)	Anglo-Saxon *seolfor*	Ag	107.88	107.110	I.
Iridium	L. *iris*, a rainbow	Ir	193.10	191.700	II., III. or IV.
Platinum	Span. *platina*, dim. of *plata*, silver	Pt	195.00	193.400	II. or IV.
Gold (*aurum*)	Anglo-Saxon	Au	197.20	195.700	I. or III.

CHLORIN (Chlorum)

Symbol, Cl. Atomic weight, 35.46.

This element occurs in nature chiefly in common salt (sodium chlorid), of which it constitutes more than one-half by weight.

Preparation.—Chlorin is prepared on a large scale by electrolysis of a solution of potassium or sodium chlorid. Chlorin separates at the anode and hydrogen at the cathode; the sodium as hydroxid remains in solution.

$$\underset{\text{Sodium chlorid.}}{NaCl} + H_2O = \underset{\text{Sodium hydroxid.}}{NaHO} + H + Cl.$$

For experimental purposes chlorin is prepared from sodium chlorid by first displacing the sodium with hydrogen to make hydrogen chlorid (hydrochloric acid), and then, by means of the oxygen of manganese dioxid, abstracting the hydrogen to form water. The first step is taken by the action of sulphuric acid:

$$(1)\quad \underset{\text{Sodium chlorid.}}{2NaCl} + \underset{\text{Acid sulphuric.}}{H_2SO_4} = \underset{\text{Sodium sulphate.}}{Na_2SO_4} + \underset{\text{Hydrogen chlorid.}}{2HCl}$$

In the second stage the HCl is broken up by the rich supply of oxygen in the manganese salt:

(2) $4HCl + MnO_2 = MnCl_2 + 2H_2O + Cl_2.$

Manganese dioxid. Manganese chlorid.

A better method is to perform both stages at once by heating in a flask over a sand-bath a mixture of sodium chlorid and granular manganese dioxid, 5 parts of each, with 12 parts of sulphuric acid and 6 parts of water previously mixed and cooled. The gas is collected in glass-stoppered bottles by downward displacement. In this reaction all the chlorin present is evolved, since the manganese is taken up by the sulphuric acid. From *bleaching powder* (calx chlorinata) a copious supply is obtainable without heat by the action of hydrochloric acid.

$$Ca(ClO)Cl + 2HCl = CaCl_2 + H_2O + Cl_2.$$

Calx chlorinata. Calcium chlorid.

Any flask or wide-mouthed bottle will serve the purpose as a generator. It should be closed with a double-perforated stopper. Through one hole passes a dropping-funnel with stop-cock;

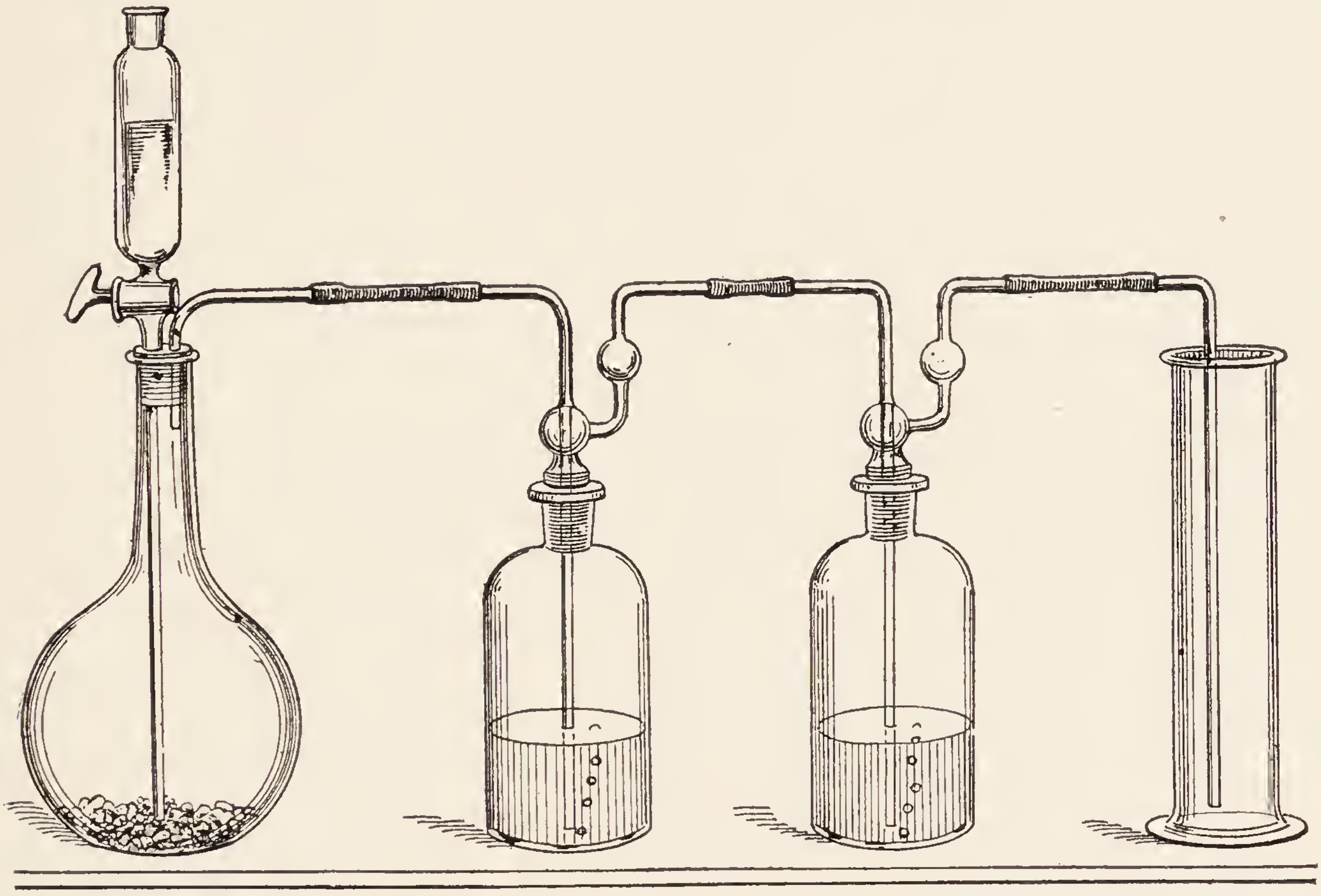


FIG. 37.—Chlorin evolved from calx chlorata washed in water and dried in sulphuric acid.

out of the other passes the delivery tube, which may enter a wash-bottle of water to get free from the hydrochloric acid fumes and another of sulphuric acid for drying; or, if absolute purity is not required, the gas may pass directly into the collecting jar. Being nearly two and a half times heavier than air, its density enables us to collect it in dry bottles by downward displacement.

When the bottle-contents are greenish yellow throughout, it should be closed with a ground-glass stopper smeared with vaselin. Its solubility in water precludes the use of the pneumatic trough unless the water be warmed. Even the mercury trough is forbidden, because it combines with the mercury.

Physical Properties.—Chlorin is a gas of a greenish-yellow color, having an unpleasant, irritating odor even when diluted with air. On inhaling, a sense of suffocation is felt in the chest and an irritation in the nose and throat, due to the corrosive action of the gas on the lining of the air-passages. Its specific gravity is 2.5. By cold [−34° C. (−29.2° F.)] and pressure it is converted into a greenish-yellow, oily liquid; and at still lower temperatures, −102° C. (−152° F.), it solidifies in greenish-yellow crystals.

Liquor Chlori Compositus, U. S. P.—*Chlorin Water.*—This is a solution of 0.4 per cent. of chlorin with potassium chlorid and chlorin oxid. It is freshly made when wanted in a 2-liter flask, by warming for three minutes potassium chlorate, 5 gm., in hydrochloric acid, 18 c.c., diluted with an equal amount of water and adding water to dissolve the greenish gas evolved.

$$\underset{\text{Potassium chlorate.}}{2KClO_3} + \underset{\text{Hydrochloric acid.}}{4HCl} = Cl_2 + \underset{\text{Chloric oxid.}}{Cl_2O_4} + 2KCl + 2H_2O.$$

One liter of water under ordinary circumstances will absorb nearly three liters of chlorin, becoming the reagent *chlorin-water.* This solution has the color, smell, taste, and chemical and therapeutic properties of the gas itself, but in a more manageable form. It should be protected from light by keeping in dark amber-colored bottles, otherwise a decomposition will occur.

In direct sunlight chlorin quickly abstracts hydrogen from the water to form hydrochloric acid, oxygen being set free.

$$H_2O + 2Cl = 2HCl + O.$$

This belongs to the class of photochemical effects, such as are seen in the processes of photography and the assimilation of carbon dioxid by green plants in the sunlight. The chemical powers reside chiefly in the blue and violet rays, which are shut out by reddish glass.

Chemical Properties.—Chlorin has an atomic weight 35.45. Like oxygen it does not burn, but at ordinary temperatures displays greater activity in supporting combustion than does oxygen. The velocity of its reactions produces sufficient heat for combustion, even when it unites spontaneously with other substances. Immersed in it, phosphorus takes fire without previous heating, powdered antimony forms a rain of sparks, and a warmed ball

of dutch-metal foil becomes incandescent.[1] Moist chlorin combines directly at room-temperature with all metals except iridium, and with most of the non-metals. In all the cases of union above mentioned the compound is a chlorid of the other element.

Toxicology.—*Symptoms.*—When inhaled in small amounts chlorin causes a suffocative feeling and cough. If taken undiluted it causes difficult breathing, a painful sense of tightness in the chest, and violent cough with hemorrhage. Indirectly the nerve-centers are involved, producing stupor and even heart failure.

Fatal Dose.—Fatal consequences are not apt to occur unless the subject is in delicate health, and the gas is taken with little admixture of air.

Treatment.—Fresh air must be given at once, and the pain relieved by the inhalation of ether. The symptoms of acute bronchitis, narcotism, and enfeebled heart action must be treated by appropriate remedies.

Detection.—The gas can be recognized by its odor and its bleaching action on moist litmus-paper. As chlorin-water it has the same properties, and in addition dissolves gold-foil.

Direct Union of Chlorin and Hydrogen.—The intense attraction that exists between hydrogen and chlorin is shown in many ways. If the two gases be mixed in equal proportions and the vessel placed in direct sunlight, a violent explosion occurs; if the mixture be kept out of strong light, the union likewise takes place, but quietly and slowly. After the union the green color is absent, and if the vessel be opened under water that liquid rises quickly in the bottle and acquires the sour taste and acid reaction of hydrochloric acid.

An ignited jet of hydrogen continues to burn when introduced into a vessel containing chlorin, the flame changing from blue to whitish green. If the vessel be afterward rinsed out with water the water will taste sour and redden blue litmus, showing the formation of hydrochloric acid.

Indirect Union of Chlorin and Hydrogen.—There are many compounds of hydrogen with carbon that lose their hydrogen in the presence of chlorin. A paraffin taper ignited will continue to burn at the mouth of a jar containing chlorin, but the carbon separates in dense clouds of soot.

$$\underset{\text{Hydrocarbon.}}{CH_4} + Cl_4 = 4HCl + C.$$

Uses in the Arts.—Although absolutely dry chlorin does not bleach, the moist vapor as a *bleaching agent* takes high rank. The native vegetable fibers are not white, and to make them acceptable to the eye linen, cotton, and paper must be bleached.

[1] In its wider sense combustion is any chemical process evolving a temperature of incandescence or 500° C. (932° F.).

A convenient source of chlorin is the bleaching powder of commerce, to be described later. Most color principles contain hydrogen, which is partly directly removed by the chlorin, but in the presence of water the action is much more decided. By decomposing the water chlorin sets free active nascent oxygen, thus becoming an *oxidizing agent.* This oxygen instantly converts sulphurous acid into sulphuric acid, a higher oxygen compound:

$$\underset{\text{Acid sulphurous.}}{H_2SO_3} + Cl_2 + H_2O = \underset{\text{Acid sulphuric.}}{H_2SO_4} + \underset{\text{Acid hydrochloric.}}{2HCl}$$

Chlorin discharges the color of common anilin inks, but does not affect the carbon of printer's ink or india ink. This can be shown by blotting a printed page with common ink and dipping it into chlorin water, when the printed letters reappear as the writing ink fades away.

As a deodorizer, chlorin breaks up the foul-smelling gases of putrefaction, hydrogen sulphid (H_2S) and ammonia (NH_3), by abstracting the hydrogen and oxidizing the sulphur and nitrogen.

As a disinfectant, chlorin poisons the bacteria that produce the infectious diseases. To do this it must be in solution, as the gas is not effectual in killing them or in materially lessening their activity. Some of the best bactericides are compounds of chlorin or its associate, iodin. It discolors and injures clothing.

Hydrogen Chlorid (HCl) (*Hydrochloric Acid Gas*).—It has been stated above that this compound can be formed by the direct union of its elements, but for laboratory purposes it is more conveniently prepared by the action of sulphuric acid on common salt (p. 135); gentle heat is required to disengage the gas HCl, leaving sodium sulphate in solution.

The gas can be prepared without heat by removing water from commercial hydrochloric acid. Using an apparatus like the generating flask, Fig. 37, nothing but concentrated sulphuric acid is placed in the flask. Gradually the hydrochloric acid is dropped in through the tap-funnel. A colorless gas is evolved which is a little heavier than the air (specific gravity 1.247), and by cold and pressure becomes first a liquid, and at $-113°$ C. ($-173°$ F.) becomes a solid. Having collected some of the gas in an inverted test-tube over a mercury trough, a few cubic centimeters of water may be blown through a bent pipet so as to rise through the mercury and make a top layer about 1 inch deep. The mercury now ascends, thus showing that the gas has been absorbed by the water. If the water were colored blue by litmus, it is turned red, and a piece of magnesium allowed to float up to the surface of the mercury, causes effervescence of hydrogen and fall of the mercury, thus showing that hydrochloric acid has been formed. The

volume of hydrogen evolved equals half that of the original hydrogen chlorid. By raising the tube out of the mercury, air enters to form an explosive mixture with the hydrogen.

ACIDS, BASES, AND SALTS

Solubility of Hydrogen Chlorid.—One of the most remarkable properties of hydrogen chlorid is its solubility in water. At ordinary temperatures 450 volumes will dissolve in 1 volume of water, evolving a large amount of heat. The heat is an indication of a special process different from simple solution. The volumes of most gases absorbed by water are not nearly so great as 450. *Henry's law* for the absorptive property of water for gases is *that the amount absorbed is proportional to the pressure* (p. 91). In the case of the absorption of hydrogen chlorid the effect of pressure is discernible only to a slight degree. These facts make it appear that the atoms of hydrogen chlorid in solution are no longer coupled as in their former condition of a dry molecule. Other evidence of a conversion is seen in the fact that pure anhydrous hydrogen chlorid compressed to a liquid has no acid properties. To develop these some new relation of its atoms is needed, and this change is brought about by the solution in water. This molecular change is explained in the following way: When the gas dissolves only a part remains as unchanged molecules, and hence subject to Henry's law. Another part is thrown into a different condition and, therefore, acquires new properties (p. 131).

Further confirmation of this view is shown in the fact that the highly volatile hydrogen chlorid in dilute solution does not lower the boiling-point of water, but raises it. This, too, is an exception to the rule for aqueous solutions of volatile substances, which usually have an opposite effect. These peculiarities in hydrogen chlorid are best explained by the theory of an abnormality in the condition and number of the ultimate particles when they are dissolved in water. Solution has apparently increased the number of particles, which could only be done by some sort of dissociation of the constituent hydrogen and chlorin in the molecules of hydrogen chlorid.

Acids.—In calling the aqueous solution of hydrogen chlorid an acid we attribute to it certain properties common to a large class. The word is derived from *acies*, sharp, and originally described the taste only. It was discovered afterward that all substances which have this taste possess a common effect upon the blue dye, litmus, turning it red (Pl. 5, Fig. 1); and further, that in the presence of metallic zinc or magnesium they yield hydrogen. Powdered magnesium will cause effervescence of the inflammable gas, not only from hydrochloric acid, but also from any acid liquid, even the juice of subacid fruits. While

hydrogen may be regarded as the element giving the acid its powers, we must not lose sight of the fact that it does not always carry this acid endowment with it. If it did, then water and the neutral compounds, alcohol, the paraffins, and fats, would be acid.

The hydrogen constituent is shown in formulas of the following strong acids: hydrochloric, HCl; sulphuric, H_2SO_4; nitric, HNO_3; phosphoric, H_3PO_4.

Bases.—An acid that tastes sour, reddens litmus, and takes a metal in place of hydrogen, loses all these properties by the addition of sodium hydroxid (caustic soda). The change in the color of acid-red litmus to blue is so sharply defined that it is customary to depend on that alone as an *indicator* of the simultaneous loss of all acid properties. If the acid be hydrochloric and litmus-paper have been used, on evaporation there is left in the dish a white crystalline compound which tastes neither sour nor alkaline, but salty. It is easily identified as kitchen salt, sodium chlorid, and is produced according to this reaction:

$$\underset{}{HCl} + \underset{\text{Sodium hydroxid.}}{NaOH} = \underset{\text{Common salt.}}{NaCl} + H_2O.$$

Neutralization.—The process just described of neutralizing the acid properties and forming water and a salt can be performed by any one of a large class of substances known as *bases*. They are compounds of metals with hydroxyl (HO), and are said to be basic because they constitute the solid residue when the more volatile acid constituent of the salt is driven off by heat. The soluble bases, of which the caustic alkalies, soda, potash, and ammonia, are the most marked representatives, are characterized by their opposition to the acids in restoring blue litmus, and in overcoming their acid taste and hydrogen-generating property. This accomplished, we have products that are neutral, such as water and common salt. In brief: *acids and bases have the power of destroying the properties of each other.*

Definite Weights Engaged.—In forming a salt, water is also a necessary product, because the hydroxyl (HO) of the base attracts the hydrogen just liberated from the acid. The numeric expression of this affinity is that the molecular weight, 17 gm., of hydroxyl in the base is required to hold the atomic weight, 1 gm., of hydrogen. Until this element is thus held the acid properties persist.

Acidimetry.—By using a solution of sodium hydroxid or potassium hydroxid of known strength we have a standard of hydrogen-fixing power, and units of it will be equivalent to definite amounts of acid in the solution neutralized. To make the two solutions of reciprocal strength and their neutralizing power equivalent to 1 gm. of hydrogen, they should be accurately tested in advance. The standard adopted is the *normal solution*, (N), for which the acid is weighed in a sufficient number of grams to

contain 1 gm. of acid hydrogen, and then dissolved in sufficient volume of water to make 1 liter of the finished product. Such a solution is sometimes called a *gram-atom*, to imply that there is in it the atomic weight of hydrogen, 1, in grams. Oxalic acid, being a crystalline solid of constant composition and easily weighed, is chosen for the acid reagent. Its formula is $H_2C_2O_4.2H_2O$, with a molecular weight of 125.7. As there are 2 atoms of acid hydrogen counted to make 125.7, the amount representing 1 atom of hydrogen would be one-half or 62.85. Then 62.85 gm. in water, to make 1000 c.c., is called the *normal solution.* If we want tc represent weak acidity, like that of the urine and gastric juice, one-tenth of 62.85 or 6.28 gm. per 1000 c.c. of solution is used, making the *decinormal* $\left(\frac{N}{10}\right)$ *solution* of oxalic acid, each cubic centimeter of which contains 0.00628 gm. of oxalic acid capable of neutralizing 0.0056 gm. of potassium hydroxid or 0.004 gm. of sodium hydroxid. The basic or alkaline solution must contain the molecular weight in grams or the exact quantity of potassium hydroxid (56 gm.) or sodium hydroxid (40 gm.) necessary to hold the 1 gm. of hydrogen that would be taken from the normal acid solution.

As the caustic alkalies contain varying amounts of water they should first be standardized by testing their concentration with the corresponding solution of oxalic acid. Thus: an excess, say 60 gm. of potassium hydroxid or 50 gm. of sodium hydroxid, is dissolved in 900 c.c. of water and tested against 10 c.c. of normal oxalic acid solution placed in a beaker and reddened with litmus to ascertain the amount of alkali necessary to neutralize it. This amount multipled by 100 gives the number of cubic centimeters of alkaline solution containing the molecular weights—56 gm. potassium hydroxid or 40 gm. of sodium hydroxid. If the amount be 9.5, then 950 c.c. will contain the *gram-molecule* amounts of alkali, and 50 c.c. of water (enough to make 1000 c.c.) must be added.[1]

A *standard* solution is one whose concentration is known.

A *normal* solution is a standard solution which contains in 1 liter the hydrogen equivalent in grams of the active reagent.

A *molar* solution is a standard solution which contains in 1 liter 1 *mole* or 1 *gram-molecular* weight of the solute.

The *normal* solution of H_2SO_4 contains $\frac{\text{mol. wt.}}{2}$, or 48.675 gm, but the *molar* solution has the full molecular weight, or 97.35 gm. of H_2SO_4 per liter.

[1] The *decinormal solution* for urine testing can be made by placing 100 c.c. of the solution just described in a mixing bottle and adding 900 c.c. of water. Or the whole operation can be changed by dividing the weights named above by 10, so that at last we have 5.6 gm. of potassium hydroxid, or 4 gm. of sodium hydroxid, in 1000 c.c. of water (pp. 559, 599).

Equivalents of Acids and Alkalies.—The label of the bottle containing the normal solutions may then state that 1 c.c. of the contents (NaOH or KOH) is the equivalent of—

Hydrochloric acid, HCl	0.03618 gm.
Nitric acid, HNO_3	0.06289 "
Sulphuric acid, H_2SO_4	0.04867 "
Oxalic acid, $H_2C_2O_4.2H_2O$	0.06285 "

The label of the normal oxalic acid solution may state that 1 c.c. of the contents is equivalent to—

Ammonia, NH_3	0.01693 gm.
Sodium hydroxid, NaOH	0.040 "
Potassium hydroxid, KOH	0.056 "

Volumetric Analysis.—If it be desired to determine the percentage of hydrogen chlorid dissolved in a sample of hydrochloric acid, 3.65 gm. of the sample are weighed, put into the beaker, and tested by adding normal solution of potassium hydroxid to neutralization. If it require 10 c.c. of KOH, then the acid liquid is a 10 per cent. solution, HCl (the *acidum hydrochloricum dilutum.*—U. S. P.). If only 9 c.c. sufficed, then the sample was 9 per cent. HCl, and is not concentrated to the official standard. Volumetric analysis is performed very rapidly, and in most cases the result is more accurate than if obtained by the tedious operation of precipitation, filtration, drying, and weighing known as the *gravimetric* method. Unless the chemist has had much experience he will obtain more accurate results by measuring quantities with a buret than by weighing them on a balance. This operation of measuring by volumetric analysis is called *titration*, from the French word *titre*, referring to the special label stating the standard strength of solution and its equivalents.

Besides the reciprocal determination of acids and alkalies, the other principal volumetric operations are *oxidation* and *reduction* (using permanganate for oxidizing and oxalic acid for reducing); *precipitation* (chlorids by silver nitrate); and *iodimetry* (reaction of iodin and hyposulphite).

Fig. 38.—Pipet for measuring.

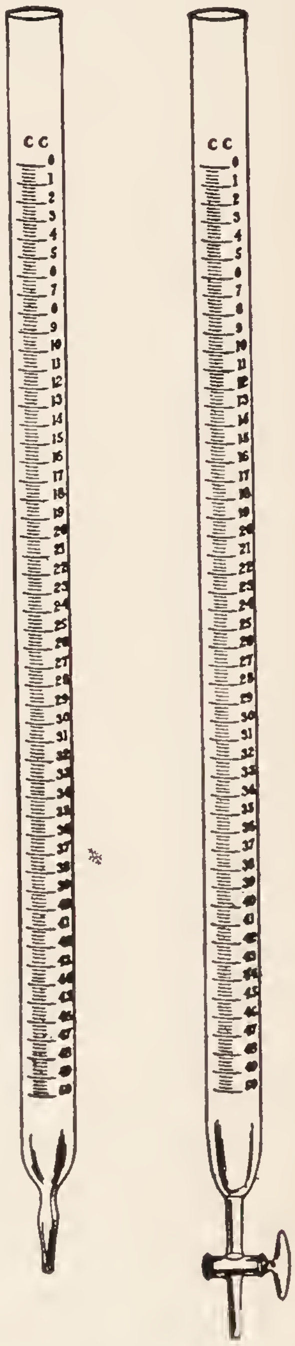


Fig. 39.—Mohr's burets.

Method of Titration.—A definite amount of the substance to be examined is measured off in a graduated pipet (Fig. 38) and placed in a small beaker or porcelain capsule. A few drops of the color indicator is then added, so that the point of neutralization or end of the reaction can be accurately determined. Litmus has been mentioned as an indicator, but *phenolphthalein* (1 per cent. in dilute alcohol) is very sensitive, and may be used when neither ammonia nor bicarbonates are titrated. It is colorless in acid fluids, but reddens by alkaline hydroxids and carbonates, but not by bicarbonates (Pl. 6, Figs. A, A′). The reagent is measured in a *Mohr's buret*, a glass tube 1 to 2 cm. in diameter, graduated in cubic centimeters and tenths, and closed below by a tap (Fig. 39). When supported upright the lower end is a narrow-pointed jet, connected by a short joint of rubber tubing, closed by a spring pinch-cock. If the reagent be affected by the rubber, as in the case of silver nitrate or potassium permanganate, then a glass cock takes the place of the rubber and pinch-cock. The reagent for acidimetry, normal solution of sodium or potassium hydroxid, is poured into the buret until it rises above the zero mark and then, placing the bottle at the tap, the reagent is run out until the mark is reached; thus the tap and jet are filled. Placing the beaker to catch the outflow, the alkaline solution is run into the mixture of acid liquid and indicator, which is constantly stirred until the end of the reaction is indicated by the change of color (pp. 559, 598).

Alkalimetry.—If the sample be alkaline urine, the degree of alkalinity is determined by placing decinormal acid in the buret, and tinting the urine with blue litmus or red phenolphthalein. If ammonia be the cause of the alkalinity, *methyl orange* is the best indicator. The acid is dropped into the urine until the end-point is shown by the color change. If the acid used number 8.3 c.c., then $8.3 \times 0.004 = 0.0332$, the alkalinity of 50 c.c. of urine, equal to 0.0664 gm. of sodium hydroxid in 100 c.c. of urine.

DISSOCIATION

From the statements on p. 123 it is clear that the hydrogen of acids is not like other hydrogen, such as that of water; the hydroxyl of bases is different from the same group in other compounds, such as in hydrogen peroxid. The chlorin of the solution of common salt in precipitating the silver from the silver nitrate shows a property shared by other chlorids, but peculiar to chlorin in a salt formed by hydrochloric acid, not possessed by the chlorin in many others of its compounds. This property is independent of the nature of the metal in the chlorid. On the other hand, the metal of the solution of base or salt shows by its reactions that its

properties do not depend upon the other components. This ability of each component to act by itself can be explained by the theory that in solution there is a detachment of the hydrogen and chlorin of hydrochloric acid; of the sodium and chlorin of common salt; of the hydroxyl and sodium of caustic soda. Strong confirmation of this view is obtained on consideration of the following experiments:

Electrolytic Dissociation.—If an electrolytic cell be made with two electrodes of platinum, connected with three or four battery couples having a galvanometer or an electric bell in the circuit, we can test the *conductivity* of different solutions in the glass cell. If pure water be put in the cell it does not conduct the electric current; therefore, the bell does not ring nor the needle of the more sensitive galvanometer oscillate. If hydrochloric acid, common salt, or sodium hydroxid be added, the current flows and is announced by the ringing of the bell or the oscillation of the needle. If the experiment be made with hydrochloric acid in a voltameter (Fig. 40), it will be observed that while the current is conducted hydrogen gas escapes at the cathode (negative pole) and chlorin at the anode (positive pole). The cathode gas may be lighted at the tap; the anode gas bleaches a piece of wet litmus-paper.[1]

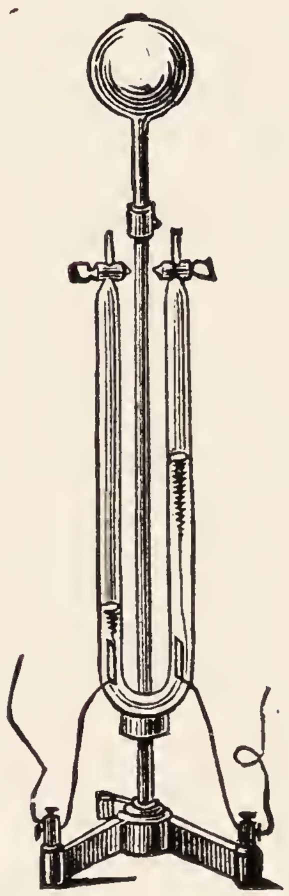


Fig. 40.—Voltameter.

Electrolytes and Ions. — Substances which in solution conduct the current and are broken up by it are called *electrolytes.* The components into which they are decomposed were called by Faraday *ions* (*movers*) (p. 50). The best electrolytes are those very acids, bases, and salts we have been studying. Close observation teaches us that there is a perfect correspondence between their conductivity and their chemical activity. They are believed to conduct the electricity only by the free ions, those that seek the cathode, such as hydrogen and the metals, being called *cations;* those that go to the anode like chlorin and hydroxyl, *anions.* The cations are supposed to carry the positive electricity to the cathode, deliver their charge, and, uniting with like atoms, become molecules; the anions do the same work for the negative electricity and resume their ordinary

[1] The best results are obtained by filling the voltameter with a mixture of one part of hydrochloric acid to six of a saturated solution of sodium chlorid. The chlorin does not appear as a free gas until the liquid at the positive end is saturated with it.

form. Electrolytes behave as if their ions differed from the same elements or compounds in their ordinary state in being energized by electric charges which they are free to carry to the electrodes. This may be indicated by separating the symbols with a comma and writing above them the signs of positive and negative electricity; or by using the round point for the cation, and the accent marks for the anions, as follows:

HCl	dissociates into		H^+, Cl^- or $H^{\cdot}, Cl'$
NaOH	"	"	$Na^+, (OH)^-$ or $Na^{\cdot}, (OH)'$
NaCl	"	"	Na^+, Cl^- or $Na^{\cdot}, Cl'$
H_2SO_4	"	"	$H^+, H^+, (SO_4)^=$ or $H^{\cdot}, H^{\cdot}, (SO_4)''$.

These are illustrations of the first mode of ion formation; *i. e.*, by the molecules in solution breaking down directly into an equivalent number of anions and cations.

The ion reaction between dilute hydrochloric acid and a weak solution of the base, sodium hydroxid, forming a salt, sodium chlorid and water, is shown in either of the following equations:

$$H^{\cdot}, Cl' + Na^{\cdot}, (OH)' = Na^{\cdot}, Cl' + H_2O$$

$$H^+, Cl^- + Na^+, (OH)^- = Na^+, Cl^- + H_2O.$$

The ions of hydroxyl and hydrogen unite and neutralize each other to form undissociated water, but the ions of sodium and chlorin retain their charge and their characteristic reactions.

Definitions.—An *acid* is a compound of hydrogen, which parts with its hydrogen in exchange for a metal, forming a salt. It is acid because when dissolved it yields hydrogen as cation. If the anion is simple the acid is *binary*, as H^+, Cl^-, if it is complex the acid is *ternary*, as $H^+, H^+, (SO_4)^=$.

A *base* is a compound of hydroxyl which neutralizes an acid forming a salt and water. It is basic because when dissolved it yields hydroxyl as anion. The cation is usually a simple metal. Bases are all ternary, as NaOH.

A *salt* is a compound formed by the action of an acid upon a base or a metal. It is a compound of the anion of an acid with the cation of a base.

The *substitution* of a metal for the hydrogen of an acid is represented in the following equation:

$$\underset{\text{Atom.}}{Zn} + \underbrace{H^+, Cl^- + H^+, Cl^-}_{\text{Ions.}} = \underset{\text{Ions.}}{Zn^{++}, Cl^-, Cl^-} + \underset{\text{Molecule.}}{H_2}$$

The *divalent* zinc (p. 114) takes two positive charges from the monovalent hydrogen ions, becoming itself an ion carrying two charges, while the hydrogen ions having lost their charge, form the neutral molecule.

The Ions of Indicators.—The characteristic changes in litmus and phenolphthalein caused by acids and alkalies find an explanation in the theory of a difference of color between the molecule of the indicator and its ion. Red is the color of the acidic molecule of litmus, which, being weak, is scarcely dissociable. When the acid litmus is neutralized by an alkali, a salt is formed and the blue anion of litmus is set free. Phenolphthalein is also weakly acidic and, therefore, not dissociable. In this molecular state it is colorless when it is added to water or to the aqueous solution of a strong acid. In the process of titration a strong base is added until the free acid is neutralized. At this point one more drop of the alkali unites with the acidic phenolphthalein and forms a dissociated salt, of which the complex organic anion has a red color.

Hydrolysis.—Weak acids and weak bases do not give a sharp change in color because, when dissolved, the salt of a weak base, like ammonium chlorid, or of a weak acid, like sodium hypochlorite, does not break up into the cation of the metal and the anion of the other component, as does sodium chlorid, but into the corresponding free acid and free base. To do this the water itself breaks up very slightly into H^+, $(OH)^-$, yielding, on the one hand, H^+ to make the acid $HClO$, and on the other, $(OH)^-$, which always gives the alkaline reaction. The salt is said to be *hydrolyzed* because there is decomposition through the agency of water. The solution behaves as if the acid and base had not neutralized each other, each giving its own reaction. Weak bases do not give a sharp reaction to litmus or phenolphthalein, as they do not suddenly free the litmus in a deep blue, and the other indicator in a marked red color, but form hydrolyzed salts with the indicators, producing gradual changes of tints. Hence, in titrating for weak acids, litmus and a strong base, sodium or potassium hydroxid, are used. In such a case, if phenolphthalein be used and the weak acids—carbonic, phosphoric, or carbolic—be titrated, a slight change of tint begins and deepens slowly before the acid has been neutralized. Nor does it act sharply in the opposite case when ammonia is titrated, because that is a weak base permitting hydrolysis. The practical conclusions are: (1) For weak acids a weak acidic indicator, like litmus, may be used, but it must be titrated with a strong base. (2) For weak bases, like ammonia, a strongly acidic indicator, like methyl orange, is required, and the titrating reagent must be a strong acid. In the

acidic molecule methyl orange is red, but converted by a base into a dissociated salt, its anion is yellow.

Ionization by Fusion.—As the temperature rises, many solid substances increase in electric conductivity and when melted become so highly ionized as to conduct freely and undergo electrolysis. Many metals are now separated from their fused compounds by electricity.

Nomenclature of Ions.—For convenience of description of the reactions of ions, special terms have been devised, based on a system. The ion of hydrogen is called *hydrion*, and other cations have their names likewise formed from the stem of the scientific name of the metals and the suffix *-ion*. The ion of hydroxyl is called *hydroxidion*, and other anions are named likewise according to the salt, those ending in *-id* or *-ide* having the suffix changed to *-idion*. For example: the chlorin ion is called *chloridion*. When the name of the salt ends in *-ate*, the corresponding ion has the suffix *-anion*. For example: in potassium chlorate the two ions are called *potassiom*, K^+, and *chloranion*, $(ClO_3)^-$; the anion of carbonates, $(CO_3)^=$, is *carbanion*. If the name of a salt end in *-ite*, the termination of the name of its anion is *-osion*. For instance: in the salt sodium hypochlorite we have *sodion*, Na^+, and *hypochlorosion*, $(ClO)^-$.

Summary of the Ion Theory.—It has been shown that when hydrogen chlorid is dissolved in water the new powers of hydrochloric acid are developed, the elements showing a different energy from that displayed by them in the dry gaseous state. These new powers in HCl may be accounted for upon the theory that the ionized elements receive a new charge of electricity when the molecules are broken up, and possess a much greater freedom of action than did the atoms in the molecule. The current conducted by an electrolyte is transported by the simultaneous movement of the component ions. The quantity carried is proportional to the number of and the valence of the ions. Chemical diversity is regulated by electric relations. Electric conductivity of a solution should be proportional to its number of free ions; and *vice versa*, the number of free ions can be estimated by measuring the conductivity. It would follow also that the total number of particles—that is, molecules of NaCl and ions of Na^+ and Cl^- in a normal solution of common salt would be larger than if none of the molecules had been dissociated. As the molecules in a normal solution of a non-electrolyte, like sugar, are not dissociated, they do not form so many particles as do the electrolytes.

In previous sections (pp. 37 and 96) it has been stated that acids, bases, and salts in aqueous solution have more effect upon the freezing-point, the boiling-point, and the osmotic pressure than

have sugar, glycerin, urea, and other non-electrolytes when dissolved in equivalent amounts. These and other physical abnormalities are correlated with the peculiar chemical and electrolytic behavior of electrolytes. The changes of energy in dissolving a substance correspond to the number of particles dissolved; and the number of free ions in solution is indicated by the electric conductivity. From this relative number of free ions we estimate the total relative number of all particles, molecules plus ions, and with this total calculate the lowering of the freezing-point and elevation of the boiling-point. On comparing the calculated results with the observed facts so close a mathematic agreement is found that we can not escape the conclusion that the theory of ion dissociation is well founded, for it has harmonized phenomena widely at variance with one another and has furnished to practical science working principles of real value. The liquid in which the life functions of plants and animals are performed is invariably a dilute electrolyte with a high degree of dissociation of ions. By applying the new conception to the sciences growing out of chemistry it has made intelligible many hitherto unexplained facts in analysis, in color-changes of indicators, in physiology, in bacteriology, and in toxicology.

Dissociants.—Of the whole number of molecules dissolved, only a fraction are usually dissociated. The number in this fraction depends on the nature of the solvent and the concentration. All liquids that are solvents of acids, bases, and salts will also dissociate their molecules to some degree. By using the methods before mentioned for measuring dissociation—that is, by freezing-point, boiling-point, and electric conductivity—it is ascertained that water has more dissociating power than any other liquid. Methyl alcohol has from one-half to two-thirds the dissociating power of water, ethyl alcohol not more than half that of methyl alcohol, or about one-fourth that of water. The hydrocarbons, ethers, aldehyds, esters, and other derivatives are weak dissociants.

Effect of Solution.—Mention has been made of the fact that when tested apart from a solvent acting as dissociant, dry chlorin does not bleach nor act on sodium, and dry hydrogen chlorid does not redden litmus nor liberate hydrogen in the presence of metals. Other experiments concur with these to show that molecules, when whole, act very little, if at all; it is only as they are broken up into ions that their chemical energies come into play. In the electrolytes, which react with promptness, there are many ions; in non-electrolytes, such as the organic bodies, sugar and albumin, there are few ions, and their reactions are much slower.

Effect of Concentration.—The *degree of dissociation* or the fractional number of ions depends mainly on the concentration.

As the relative conducting power of electrolytes rises with the dilution up to a certain limit, it is assumed that when this highest point is reached dissociation is complete. When the strong acids, bases, and salts are in very dilute solution it is highly probable that the relatively few molecules have all been dissociated. It is discovered that at this point of highest conductivity the acids, bases, and salts are most active chemically—that is to say, that the millenormal $\left(\frac{N}{1000}\right)$ solution of HCl has more than $\frac{1}{1000}$ the activity of the normal (N) solution.

Strength of Acids.—As stated above, experiment shows that the relative electric conductivities of acids vary as do their chemical activities. When *hydrochloric acid* has been diluted until it is a $\frac{N}{1000}$ solution, the high conductivity makes it probable that its molecules have nearly all been separated into free ions, but the $\frac{N}{1000}$ solution of *acetic acid* has not reached its highest conductivity, and is believed, therefore, to have but few dissociated ions. When zinc is put into equal volumes of decinormal $\left(\frac{N}{10}\right)$ hydrochloric and acetic acids separately, they will each dissolve the same weight of metal because each contains the same quantity of acid hydrogen. But the velocity of their action is very different, hydrochloric acid finishing its work much sooner; hence it is said to be more *active*. Nearly all the hydrogen of hydrochloric acid is at once available, little of it being held in molecules, but with acetic acid some of the hydrogen ions must escape before the many undissociated molecules dissociate into active ions. In other words, the *strongest* acid chemically is the one that is most dissociated, having the highest proportion of free hydrogen ions. The degree of dissociation of the following acids is about 70 per cent. in a $\left(\frac{N}{10}\right)$ solution; they are very active and are called the *strong* acids, *i. e.*, hydrochloric, hydriodic, hydrobromic, chloric, perchloric, sulphuric, polythionic, and nitric. Usually sulphurous, phosphoric, and acetic acids are not dissociated beyond 10 per cent. and are called moderately strong. A dissociation of less than 1 per cent. characterizes as *weak* the acids sulphydric, carbonic, hydrocyanic, silicic, and boric.

Analysis.—The first act in the analysis of salts is dissolving them in water. In solution they dissociate into their components, the metal and the residue derived from the acid; these have individual reaction. As stated above, the chlorin in chlorids has

a peculiar reaction with silver nitrate irrespective of the metal with which it is united, and different from that in the chlorates. So it is with iodids, sulphates, and other acidulous factors of salts. The metal in its turn is sought independently, regardless of the other constituents. The salts formed by copper with the different acids will yield to hydrogen sulphid the same black precipitate. The first step of dissolving the salt separated its component ions to such a degree that the behavior of each became independent of the other.

Mixed Solutions.—When solutions of acids, bases, and salts are mixed without precipitation the free ions of all of them are contained in the mixture and can be identified by individual tests; no matter how they were arranged in the original salt. Thus: When equivalent amounts of sodium chlorid, $NaCl$, and potassium iodid, KI, are mixed in solution they evolve no heat and give exactly the same reactions as does a mixture of potassium chlorid, KCl, and sodium iodid, NaI. When some of the mixed ions can unite to form an insoluble compound they do so with heat changes, forming a precipitate. Thus: mixed solutions of potassium iodid, KI, and lead nitrate, $Pb(NO_3)_2$, develop heat and separate out the undissociated solid lead iodid, PbI_2.

Ions of Consummated Reactions.—The reaction between two active substances begins as soon as they are brought together. The initial velocity depends on the temperature and the concentration (mass) of the solutions. This movement gradually declines until the *factors* and the *products* reach a certain concentration, when a condition of equilibrium is established between the direct and the reverse tendencies (p. 83). In an operation where one of the reacting products escapes so fast that its acting mass is never present as part of a system in equilibrium, the direct action goes on to completion thus:

1. The gas hydrogen is set free from an acid by the substitution of a metal (p. 80).

2. A volatile product is distilled away by heat as in the preparation of hydrochloric acid (p. 136).

3. An insoluble product is precipitated by the combination of dissolved ions into molecules, as when silver nitrate is acted upon by a chlorid, and silver chlorid thrown out of solution.

$$Ag^+, (NO_3)^- \quad + \quad Na^+, Cl^- \quad = \quad AgCl \quad + \quad Na^+, (NO_3)^-.$$

4. The ions of a metal in solution are deposited as atoms by electric action, as in plating with copper.

$$Cu^{++}(SO_4)^= \quad + \quad H_2O \quad = \quad Cu \quad + \quad H^+{}_2(SO_4)^= \quad + \quad O.$$

Applications in Toxicology.—The poisonous properties of many compounds are not the sum of those of the elements composing them. In this matter the compound does not act as a whole, nor do the elements as individuals, unless they have been ionized. A solution of potassium cyanid is very poisonous, but one of potassium ferrocyanid is not, and yet cyanogen is in both. In the first named the poison exists as cyanidion, $(CN)^-$, formed when the salt is first dissolved. In the second named, which contains iron and cyanogen, there is no exhibition of the chemical or toxic reactions of either, because the cation is potassion, and the anion is more complex than ferrion, Fe^+, or cyanidion, $(CN)^-$, being $[Fe(CN)_6]^{\equiv}$, ferrocyanidion, entirely devoid of poisonous properties (pp. 199, 345).

Silver salts are reduced in toxic effect by the addition of sodium thiosulphate; argention, Ag^+, is lost in a new complex ion, $(AgS_2O_3)^-$, which is non-toxic, as it does not exert the same activity as Ag^+.

The caustic alkalies disorganize and dissolve tissue by virtue of the hydroxidion $(HO)^-$ and not because of the metal, for sodium chlorid contains the metal, but is not poisonous. Hydroxyl undissociated is not poisonous, for if it were, alcohol in aqueous solution would corrode, as it contains that group, though not in the state of ion.

The sulphates of potassium, sodium, and magnesium in concentrated solution are active cathartics. They have in common the group $(SO_4)^=$, sulphanion, and they are all irritants. It is a fair presumption that the metal cations take no part here; their local effects are indifferent in their other compounds. The bowel irritation and the griping caused by the sulphates are proportional to the relative amount of sulphanion, which in equal doses is greatest in potassium sulphate, K^+, K^+, $SO_4^=$, molecular weight 174, in water dissociating 53 per cent. $(SO_4)^=$, rich in ions, with correspondingly high osmotic pressure, and least in the magnesium salt, Mg^{++}, $SO_4^=$, $7H_2O$, molecular weight 246, dissociating less $(SO_4)^=$, fewer ions, and therefore having lower osmotic pressure.

HYDROCHLORIC ACID (Acid Muriatic)

Formula, HCl. Molecular weight, 36.45.

Preparation.—The commercial muriatic acid not infrequently contains a trace of arsenic. As it is easier to obtain arsenic-free sulphuric acid, the analyst sometimes makes for himself the hydrochloric acid he intends to use in detecting arsenic. Fifty grams of pure common salt are put into a flask or retort and then is added through a funnel tube dilute sulphuric acid, which has been mixed in advance and allowed to cool. To make dilute

sulphuric acid 30 c.c. of the pure acid is diluted with 10 c.c. of water. If gas does not immediately escape, gentle heat may be applied (Fig. 41). The gas is passed into a suitable wash-bottle in order to charge the distilled water it contains.

$$\underset{\text{Sodium chlorid.}}{NaCl} + \underset{\text{Sulphuric acid.}}{H_2SO_4} \rightleftarrows \underset{\text{Acid hydrochloric.}}{HCl} + \underset{\text{Sodium bisulphate.}}{HNaSO_4}$$

This is a reversible equation, and in the cold an equilibrium is set up among the four substances dependent on the quantities. When part of the volatile HCl escapes by heat the equilibrium is destroyed and action goes on to make fresh HCl.

Official Preparations.—*Acidum hydrochloricum* contains 31.9 per cent. by weight of anhydrous HCl. Dose: 3 to 10 ♏ (0.20–0.66 c.c.), well diluted; incompatible with alkalies, chlorates, chromates, salts of silver, mercury, and lead, oxids, permanganates, tartar emetic. *Acidum hydrochloricum dilutum*, contains 10 per cent. by weight of anhydrous HCl. Dose: 10 to 30 ♏ (0.66–2 c.c.), well diluted with sweetened water.

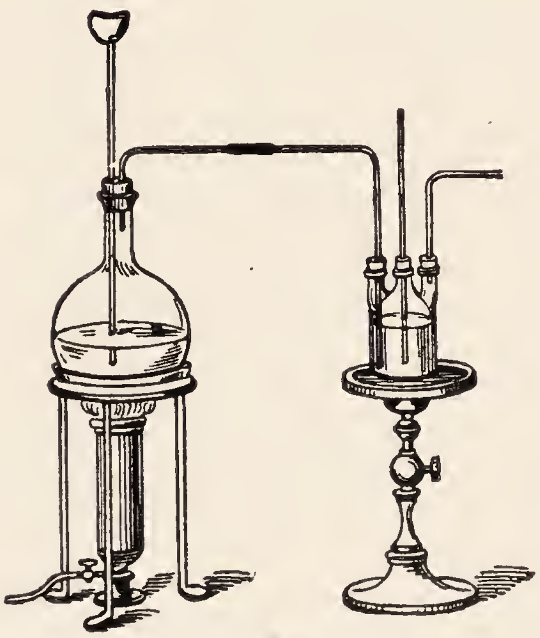


FIG. 41.—Charging water with soluble gas.

Properties.—Commercial hydrochloric, or muriatic acid is a transparent, yellow, corrosive liquid. Its strength or percentage of pure acid gas is approximately the product of 200 and the decimals of the specific gravity. Thus, a sample of a specific gravity of 1.15 should contain 30 per cent. HCl (200×0.15).

The chemically pure acid is colorless, the yellow color of the commercial article being due to a trace of iron from the apparatus used in its manufacture. A more important contaminant is arsenic, taken from the sulphuric acid used in generating it. The average amount of this impurity is 0.25 per cent. of arsenic trioxid. The pure acid liquid of the U. S. Pharmacopœia is sour, of pungent odor, and contains 450 volumes of gas dissolved in 1 volume of water, which increases more than one-third in bulk.

On exposure to the air the strong acid gives off visible fumes, due to the union and condensation of the invisible gas with the aqueous vapor of the air. The fumes have a pungent odor, an acid taste, are irrespirable, are one-fourth heavier than the air, and when allowed to blend with the fumes of ammonia form dense white clouds of ammonium chlorid. It acts upon metals and

bases, forming chlorids. The acid dissolves most of the metals, but not gold and platinum, and when heated with manganese dioxid, chlorin is set free. It is the natural acid of the gastric juice, and is used with pepsin as an aid to digestion. It is employed in chemical analysis as a group-reagent, from its having the property of precipitating mercury (from mercurous salts), lead, and silver.

The precipitation of silver salts occurs according to the following equation:

$$\underbrace{Ag^{+}, (NO_3)^{-}}_{\text{Silver nitrate ions.}} + H^{+}, Cl^{-} = \underbrace{AgCl}_{\text{Silver chlorid molecules.}} + \underbrace{H^{+}, (NO_3)^{-}}_{\text{Acid nitric ions.}}$$

When the ions of the first half of an equation can unite to form an insoluble molecule, the union occurs and a precipitate falls. This precipitate, AgCl, is soluble in ammonium hydroxid, but insoluble in nitric acid. A similar precipitate of mercurous chlorid turns black with ammonium hydroxid, while that of lead chlorid under the same conditions remains white and undissolved.

Toxicology.—The Corrosive Acids.—The mineral acids: hydrochloric, sulphuric, and nitric, turn red the vegetable blue colors, and change the hue of dyed clothing mostly to red or yellow, and also injure the texture. When concentrated, they rapidly destroy organic substances, and on the living body cause the most violent pain. They are simple corrosives, causing well-marked symptoms, due to their action on the part to which they are applied, complicated by the effects of shock upon the system at large.

Hydrochloric acid is very corrosive, but not so severe in its local action as either sulphuric or nitric acid. Owing to its volatility there is great liability of acute laryngeal inflammation from its irritating fumes, although the liquid itself may not enter the glottis. The lips, tongue, and throat are first white, but later become brown and rotten. There are instant pain in the mouth, throat, and abdomen, difficult swallowing, husky voice, spasmodic breathing, retching and vomiting, feeble pulse, and general weakness, the mind remaining clear to the last. If the patient survive these acute symptoms, he remains subject to stricture of the gullet or pylorus, with loss of function of the stomach.

Fatal Dose.—A few drops may prove fatal if they enter the larynx. By rapid swallowing and quick transmission to the stomach death may follow upon a fluidram dose.

Fatal Period.—From the acute effects death may ensue in fifteen hours or even in two hours, but, as a rule, the duration of life will be twenty-four hours. The secondary consequences are productive of a poor vitality for a variable period. One case

has been reported of death from stricture of the pylorus after four months.

Treatment.—The remedial measures are the same for hydrochloric as for sulphuric and nitric acids.

The antidotes owe their power to chemical neutralization, changing the fiery acid to harmless neutral salts.

Calcined magnesia, given freely, suspended in water or milk, is a perfect antidote. When it cannot be had at once, as promptness is all-important, "prepared chalk," "whiting" used to polish silver, plaster scraped from the wall, soapsuds, or largely diluted alkalies, such as sodium carbonate ("washing-soda"), sodium bicarbonate ("bread or baking-soda," "saleratus"), sodium hydroxid ("concentrated lye"), or the corresponding compounds of potassium, should be given in milk or water. It rarely happens that the antidote is given soon enough to prevent the energetic action of the poison, and even after thorough neutralization it would be best to give milk and very dilute alkaline solutions for some hours. As the tube of the stomach-pump or the siphon impinging upon the softened structures may do irreparable harm, it must not be used, though later the esophageal stricture may call for careful treatment by dilator and tubes.

Postmortem Appearances.—The pathologic changes found after death from hydrochloric acid cannot be distinguished from those induced by sulphuric acid, except by the local effects on lips and face.

Hydrochloric acid leaves no permanent stain nor erosion externally, while sulphuric acid discolors and nitric acid turns yellow. Internally, we find the signs of intense inflammation, with a shriveled and worm-eaten condition of the mucous membrane, which has a white or brownish color. The appearances due to sulphuric acid are the same, except that the destruction of tissue is greater, but the yellow marks of nitric acid are always characteristic.

Tests.—The free acid gives the acid reaction to litmus. A glass stopper or rod wet with it and held near an open bottle of ammonia-water smokes with the white clouds of ammonium chlorid. Poured upon zinc, it evolves hydrogen gas; if heated with manganese dioxid, it yields greenish-yellow chlorin gas which bleaches a piece of moist litmus-paper suspended in the vapor.

Silver Nitrate Test.—The chief test for chlorids serves equally for this acid—that is, silver nitrate—which gives a heavy, curdy, white precipitate of silver chlorid, soluble in ammonium hydroxid, but insoluble in nitric acid.

As proof of the presence of a *free mineral acid*, litmus will not serve, as it is affected by acid salts and by the organic acid of

digestion. Resort can be had to paper colored by certain anilin dyes which react to minute quantities of free mineral acids, but not in the same way to the organic acids nor to acid salts. A drop of the gastric contents containing a free mineral acid put on Congo-red paper leaves a dark-blue spot (Pl. 5, Figs. 2–4) or if touched to Töpfer's yellow reagent turns it red (p. 557, Plate 6, Fig. *C*).

Detection.—Very little help is derived from a study of the stains on clothing. At first a reddish spot appears. On some black dyes the color is greenish, but owing to the volatility of the acid, the spots are evanescent. They are not moist, charred, nor rotten, as they are from sulphuric acid, nor are they yellow, as from nitric acid. After a few days the moistened cloth will not affect litmus, but if boiled in water, silver nitrate will show more chlorids in it than in the untouched cloth.

In the examination of the vomited matters we are liable to a fallacy from the natural presence of 0.2 per cent. of hydrochloric acid in the gastric juice, and from the chlorin in the alkaline chlorids of food.

If the material be strongly acid, sulphuric acid must first be tested for and excluded. Distillation will then collect the volatile hydrochloric acid, which can be estimated by titration with sodium hydroxid.

To determine both free acid and the combined chlorids, first make a filtered watery extract and divide it into two equal parts. One of these is neutralized by adding an excess of sodium carbonate, which fixes the volatile free acid. Both are evaporated to dryness, the unneutralized portion losing all its free acid. Both residues are redissolved in water and are treated separately with acid solution of silver nitrate. If the neutralized portion show more chlorids than the other, the difference equals the amount of free hydrochloric acid originally present in each portion. In this analysis 100 parts of silver chlorid precipitated represent about 80 parts of hydrochloric acid (specific gravity 1.15) or 25.43 parts of the anhydrous acid.

COMPOUNDS OF CHLORIN CONTAINING OXYGEN

Chlorin and oxygen form two compounds—chlorin monoxid, Cl_2O, and chlorin tetroxid, Cl_2O_4—both of which are unstable and at times violently explosive. They are present dissolved with free chlorin in *liquor chlori compositus* (p. 120). They have no special uses in medicine or in the arts of everyday life.

An acid formed with hydrogen and without oxygen is known as a *hydracid*. To this class belong HCl, HBr, and HI. When oxygen is a constituent, the acid is termed an *oxyacid*. There

are many representatives of this class, and among them are the four oxyacids of chlorin, which illustrate well the law of multiple proportion, but are quite unstable, and of little practical importance:

Hypochlorous acid	$HClO$
Chlorous acid	$HClO_2$
Chloric acid	$HClO_3$
Perchloric acid	$HClO_4$

The **nomenclature of these acids** is governed by the proportion of oxygen they contain. If there be but one acid to be named, such as hydracid HCl, the termination *-ic* is used, and its salts end in *-ate.* If there be two oxyacids, the one containing the smaller proportion of oxygen has the suffix *-ous*, as chlorous, $HClO_2$; the other *-ic* as chloric, $HClO_3$. The names of salts of acids ending in *-ous* are formed by adding to the stem the suffix *-ite.* When an element forms more than two oxyacids, the prefix *hypo-* is given to the acid having less oxygen than the *-ous* acid, as hypochlorous; and the prefix *per-* to the acid having more than the *-ic* acid, as perchloric. In the above list will be found four acids named according to this system, only two of which, however, are of interest to us—hypochlorous and chloric.

Hypochlorous Acid.—Calx Chlorinata.—When slaked lime is exposed to the action of chlorin gas for about sixteen hours, it takes up the chlorin and forms the commercial product known as *chlorid of lime*, or *bleaching powder*, the official name being *calx chlorinata* in U. S. P. Not markedly deliquescent, it probably does not contain calcium chlorid, for that compound is deliquescent to a high degree. The composition of calx chlorinata is represented by the formula Ca(ClO)Cl, or $Ca<^{Cl}_{ClO}$; and its manufacture by the equation:

$$\underset{\text{Lime.}}{Ca(OH)_2} + Cl_2 = \underset{\text{Calx chlorinata.}}{Ca(ClO)Cl} + H_2O.$$

Treated with water, calx chlorinata dissolves, changing into calcium chlorid and calcium hypochlorite:

$$2Ca(ClO)Cl = CaCl_2 + Ca(ClO)_2.$$

The bleaching action of calx chlorinata is demonstrable by smearing a printed page with writing ink, dipping the page into a dilute solution of calx chlorinata, and while wet transferring it to weak hydrochloric acid. Any textile fabric so treated will have nascent oxygen and chlorin set free in its meshes. The carbon of the printers' ink will not be affected.

$$\underset{\text{Calcium hypochlorite.}}{Ca(ClO)_2} + 2HCl = \underset{\text{Calcium chlorid.}}{CaCl_2} + H_2O + Cl_2 + \underset{\text{Nascent oxygen.}}{O.}$$

A solution of calx chlorinata, 1 pound to the gallon of water, represents in a more stable form all the disinfecting powers of *chlorin water*, and is extensively used as a deodorizer and germicide. Exposed to the air it evolves chlorin spontaneously.

When calcium hypochlorite is acted upon by very dilute nitric acid and the product distilled, dilute hypochlorous acid is obtained.

$$\underset{\text{Calcium hypochlorite.}}{Ca(ClO)_2} + \underset{\text{Nitric acid.}}{2HNO_3} = \underset{\text{Calcium nitrate.}}{Ca(NO_3)_2} + \underset{\text{Hypochlorous acid.}}{2HClO}$$

Properties.—Hypochlorous acid has not yet been formed absolutely dry. In aqueous solution it has the strong smell of chlorin, but not the greenish hue of chlorin water. It does not keep well, soon breaking up into oxygen and hydrochloric acid. As it yields a ready supply of active oxygen it has the same bleaching and germicidal powers possessed by chlorin-water.

$$HClO = O + HCl.$$

Tests.—Owing to the constant presence of some hydrochloric acid it yields a white precipitate with silver nitrate. It decolorizes litmus and indigo in solutions.

Sodium hypochlorite, $NaClO$, is known only in the official *liquor sodæ chlorinatæ*, Labarraque's fluid, which contains $NaCl + NaClO$, and is prepared by decomposing solution of calx chlorinata by sodium carbonate, or by passing chlorin into a solution of caustic soda: $2NaOH + Cl_2 = NaCl + NaClO + H_2O$. It is more permanent than chlorin-water, but undergoes a change in time, losing its chlorin smell and bleaching power and the property of yielding chlorin when treated with dilute hydrochloric acid, due to the loss of its hypochlorite. On evaporation sodium chlorid is obtained, and another salt having the composition $NaClO_3$, called *sodium chlorate:*

$$\underset{\text{Sodium hypochlorite.}}{3NaClO} = 2NaCl + \underset{\text{Sodium chlorate.}}{NaClO_3}$$

If caustic potash, KOH, had been used, then potassium hypochlorite would have formed, changing to *potassium chlorate*, $KClO_3$, a well-known salt already referred to as a source of oxygen. By electrolysis of a solution of this salt, potassion $K^{\cdot}$ moves to the cathode and chloranion $(ClO_3)'$ to the anode. As the chlorin is here part of a complex anion it is not surprising that this salt does not precipitate silver chlorid from solution of silver nitrate (p. 137).

OTHER HALOGENS

BROMIN (Bromum)

Symbol, Br. Atomic weight, 79.92.

Occurrence.—Though met in smaller quantities than chlorin, which it closely resembles, bromin is widely distributed in nature. In the residues of evaporation of sea-water bromin compounds of sodium and magnesium are found, and from these the element is liberated.

Preparation.—The reactions by which bromin is made are parallel to those used for chlorin. By electrolysis of bromids the bromidion moves to the anode and separates as free bromin, the metal going to the cathode. By another method the bromids in sea salt are in one operation converted to hydrobromic acid, and this, oxidized by manganese dioxid, loses its hydrogen, leaving free bromin.

$$\underset{\text{Sodium bromid.}}{2NaBr} + H_2SO_4 = \underset{\text{Sodium sulphate.}}{Na_2SO_4} + \underset{\text{Hydrobromic acid.}}{2HBr}$$

$$2HBr + O = H_2O + Br_2.$$

This process is facilitated by the free chlorin formed from the chlorids present in the salt; or chlorin may be obtained outside and passed into the brine. It decomposes the bromids and the bromin distils over.

Properties.—Physical.—Bromin is a dark, reddish-brown liquid, opaque in thick layers, with a specific gravity of 3.1. At ordinary temperatures it vaporizes in red fumes of an unpleasant odor and is highly irritating to the mucous membrane of the nose and air-passages. It should be held at arm's length in handling. It boils at 60° C. (140° F.) and solidifies at −7° C. (19° F.), forming a dark crystal. It is soluble in alcohol, ether, and chloroform. At room temperature it dissolves 3 per cent. in water, making a brown-yellow liquid with the properties of bromin. This solution is used as a reagent under the name of *bromin-water*. Exposed to light, bromin-water decomposes, forming hydrobromic acid. When the water already contains a bromid in solution, the bromin dissolves in larger amount, forming compounds that readily decompose and behave in a manner similar to free bromin. There is no more free bromin in solution than would be the case if water alone were the solvent, but the salt holds the bromin as the brown-colored ion, Br_3^- (*tribromidion*). In any reaction the bromid-salt solution yields fresh bromin to the water as fast as the

free bromin is removed. The ion Br^{-}_{3} splits into $Br^{-} + Br_2$, which is to say, the tribromidion yields bromidion and neutral bromin.

Chemical.—The behavior of bromin is similar to that of chlorin, but its activity is less. It is a monad, combines with many elements directly, and unites with arsenic with so much avidity as to evolve heat and light. If powdered magnesium be shaken with bromin-water the color disappears, and after filtering off the metal a solution of ($MgBr_2$) magnesium bromid remains. If this is decomposed in an electrolytic cell yellowish bromin is liberated at the anode, while at the cathode white magnesium hydroxid, $Mg(OH)_2$ and bubbles of hydrogen appear. The free magnesium has taken hydroxyl from water and set free the hydrogen.

Medical Uses.—Bromin has been given internally in doses of 1 to 3 ♏ (0.06–0.18 c.c.), well diluted; externally as an antiseptic in 1 per cent. lotions, or as caustic, used pure or with equal parts of alcohol. The alkaline bromids are given internally as sedatives, hypnotics, and antispasmodics. It is *incompatible* with caustic alkalies, arsenites, ferrous salts, hypophosphites, hydriodic acid, and mercurous salts.

Toxicology.—Symptoms.—Bromin vapor when inhaled causes symptoms of violent catarrhal inflammation of the air-passages, with cough, constriction of the chest, and hemoptysis. It acts vigorously as a caustic on organic matter, producing, when swallowed, pain in the mouth, throat, and stomach, with eructation of the peculiar offensive vapor. Its powerful local action may bring on collapse in a few hours.

Fatal Dose and Period.—Very few cases of death have been reported. One was caused by 1 oz. of bromin. In another fatal case a child of ten took what was calculated to be about 2 gr. of bromin. Fatal collapse has come on within seven hours.

Treatment.—If it has been swallowed, complete evacuation must be secured by emetics (5 ♏ of a 2 per cent. solution of apomorphin hydrochlorate) and the stomach-pump. The chemical antidotes are protectives, such as raw eggs, mucilaginous drinks made from starch, arrow-root, barley, rice, flour, or meal. If bromin has been inhaled, ammonia vapor and steam must be inhaled as antidotes. For depression whisky may be given.

Postmortem Appearances.—A dark-brown stain marks the point of local action; the mucous membrane is inflamed, softened, loosened, or even corroded.

Detection.—The element may be identified by its color and odor. If it be present as bromidion in a bromid, the bromin must be freed by adding a little chlorin-water. The chlorin becomes chloridion and the bromidion changes to neutral bromin
becomes chloridion and the bromidion changes to neutral bromin
with its characteristic brownish color, $K^+Br^- + Cl = K^+Cl^- + Br$.

When bromin-water is shaken with chloroform, the latter takes up the bromin and separates it in a brownish-yellow layer. Starch-water forms the bromid of starch, which is of a deep yellow color.

"Bromism."—This name has been given to the poisonous effects of long-continued dosing with bromids. The symptoms are the fetid odor of bromin on the breath, mental dulness, nervous depression, muscular weakness, absence of sexual feeling, eruptions of acne, bullæ, and pustules. When pushed to the extreme, the bromids have caused exhaustion and fatal heart failure.

Hydrogen bromid, HBr, is a colorless gas readily soluble in water, forming *acidum hydrobromicum dilutum* (U. S. P.), which is a 10-per cent. solution of hydrogen bromid, resembling hydrochloric acid in chemical properties, but medically having the sedative action of bromids. It is given to allay cough in doses of 30 to 90 ♏ (1.90–5.70 c.c.) in sweetened water. It is unstable.

The **bromids** in general are formed like the chlorids and have similar properties.

Like the chlorids, they are quite soluble, except the bromid of silver, the mercurous bromid, and the lead salt, which are almost insoluble. The silver bromid is insoluble in nitric acid and sparingly soluble in ammonium hydroxid.

The reaction with silver nitrate is as follows:

$$K^+, Br^- \quad + \quad Ag^+, (NO_3)^- \quad = \quad K^+, (NO_3)^- \quad + \quad AgBr.$$

The precipitate AgBr does not form unless the bromin is dissociated as bromidion. Thus in ethyl bromid, C_2H_5Br, a non-electrolyte, the bromin is not ionized and there is no reaction with the silver ion.

Oxyacids.—Three oxyacids are known and they are more permanent than the corresponding compounds of chlorin. They are *hypobromous acid*, HBrO; *bromic acid*, $HBrO_3$; and *perbromic acid*, $HBrO_4$.

IODIN (Iodum)

Symbol, I. Atomic weight, 126.92.

Occurrence.—In nature iodin is found combined with potassium, sodium, calcium, and magnesium in sea-water, in sea animals, and sea plants.

Preparation.—The ashes of the seaweed called *kelp* are extracted with water, and by evaporation the other salts crystallize out, leaving a mother liquor containing the iodids. Chlorin, obtained from bleaching powder, decomposes the iodids and free iodin distils over. With potassium iodid the reaction is:

$$K^+, I^- \quad + \quad Cl \quad = \quad K^+, Cl^- \quad + \quad I.$$

Properties.—Physical.—Iodin deviates from bromin in the same direction that bromin deviates from chlorin: chlorin is a gas, bromin a liquid, and iodin a solid. Its crystals are blue-black, soft, and scaly, having a metallic luster and an unpleasant taste. The specific gravity of iodin is 5; it melts at 114° C. (237° F.) and boils at 175° C. (347° F.). At all temperatures iodin gives off a vapor possessing a characteristic odor and a violet color, to which latter the name of the element is due (*iodes, violet*). If a large flask be strongly heated by constant turning over a large flame, and a few crystals of iodin be then thrown in, a heavy vapor of a dark violet color forms. The specific gravity of this vapor is 8.716.

The crystals are only sparingly soluble in water, but if an excess of iodin be left in the bottle in time a larger amount is taken up, some of it passing into the state of hydriodic acid (HI) by a decomposition of water similar to that caused by chlorin and bromin. This hydriodic acid assists in dissolving the iodin. If the water contain an iodid, such as potassium iodid, much larger quantities of iodin pass into solution.

This phenomenon, like a similar one described under Bromin (p. 142), is due to the formation of an easily decomposed compound, in which the colorless iodidion, I^-, of the salt becomes brown tri-iodidion, I_3^-. In using it, as fast as the free iodin is taken away, the I_3^- is broken up to I^- in the iodid and neutral iodin I_2, which replaces the free iodin in solution. This property is employed in the highly iodinized official preparations, all of which contain potassium iodid as well as iodin, *tinctura iodi, liquor iodi compositus*, or *Lugol's solution; unguentum iodi*, or *Lugol's ointment*, and also *Churchill's tincture.*

Iodin is very soluble in alcohol, forming the dark red-brown tincture (7 per cent. of iodin). When dissolved in ether it has the same red-brown color, but in chloroform, benzene, and carbon disulphid its solutions are a fine violet color. As carbon disulphid is a heavy colorless liquid not miscible with water, it may be used to show the phenomenon of separation by the difference of solubility, which is as 1 : 700. The brown solution of iodin in water loses its color when shaken with carbon disulphid, the disulphid being turned a deep violet and separating as a bottom layer. That this applies only to the elementary iodin is shown by adding potassium hydroxid to the water and shaking the fluids again. The violet color disappears from the carbon disulphid as the iodin changes to potassium iodid and passes into its better solvent, the water.

Chemical.—Closely akin to chlorin and bromin in its reactions, iodin is less active than either. It has feeble bleaching and

oxidizing powers and decomposes water slowly. Ozone forms an oxid with it, but oxygen does not. Ammonium hydroxid converts iodin into an explosive, nitrogen iodid. It is oxidized by nitric acid into iodic acid.

Amylum iodatum, or **starch iodid,** is a compound having a deep-blue color, and is formed when a cold solution of boiled starch is treated with free iodin. Although this is a compound, yet as the union is not very strong, it has to some degree the chemical and medical properties of iodin. This characteristic reaction is used to detect both starch and iodin.[1] Should the indications be doubtful, the blue fluid may be heated, when the blue starch iodid will dissociate and the brown color of free iodin appear. When cooled, the blue compound is restored.

Iodids have a resemblance to the chlorids and bromids, and are formed by similar reactions. All the metallic iodids are soluble, except those of silver, lead, and the mercurous salt. The lead iodid is feebly soluble. Chlorin displaces iodin as it does bromin.

Incompatibles.—The alkalies, alkaloids, metallic salts, starch, tannin, and turpentine.

Medical Uses.—Free iodin is a local escharotic, discutient and disinfectant. Internally, it is an alterative for scrofulosis.

Toxicology.—By mistake, though rarely, the tincture and the liniment have been taken internally with poisonous effects.

Symptoms.—It acts as a powerful irritant upon the stomach and bowels, causing pain in the mouth, throat, and stomach, vomiting and purging, extreme thirst, fainting attacks, and collapse. When applied by surgeons freely to absorbing surfaces, it may cause systemic disturbances, such as headache, dizziness, mental trouble, along with the above gastric symptoms brought about indirectly. Its elimination by the kidneys involves those organs in inflammation, which may end in suppression of urine.

Fatal Dose.—Death has resulted from 1 fl. dr. of the tincture, containing less than 2 gr. of the element. Ten or 20 gr. of the solid would probably be fatal. Recovery has followed a dose of 1 fl. oz. of the tincture.

Fatal Period.—While death has occurred in twenty-four hours, in cases of poisoning from external application it will be delayed for several days.

Treatment.—Large drafts of tepid water will assist in evacuating the stomach. The antidote is starch in some form, best given in decoction, such as the clear starch of the laundry; or as gruels,

[1] A sensitive starch paste is best made by grinding a small amount of laundry starch in a mortar with cold water and then pouring it into hot water at the boiling-point while stirring. Heat is withdrawn and after cooling the thin, clear solution detects the merest trace of iodin.

boiled rice, or arrow-root, given as long as the vomited matters have a blue color.

Postmortem Appearances.—The morbid changes found are such as attend gastro-intestinal irritation, leading to inflammation and excoriation.

Detection.—By agitating organic matters or an aqueous solution of iodin with carbon bisulphid the iodin is separated, making a violet-colored solution. If the iodin is combined, a very small quantity of chlorin-water must be used to liberate it. A decoction of starch which has been allowed to cool gives a dark-blue color, due to the formation of iodid of starch. The yellow stains on the skin and lips are removable by ammonia, which would only deepen the stain if due to nitric acid.

"Iodism."—Excessive doses of iodids or the persistent use of average doses may induce the symptoms of "iodism." These are frontal headache, catarrh, general malaise. The face swells and skin eruptions appear. Fatal cases are rare.

Hydrogen Iodid.—This is a colorless gas having the formula HI, and, like HCl, dissolves freely in water, forming *hydriodic acid.* This acid closely resembles the hydracids of chlorin and bromin, and can be prepared by passing hydrogen sulphid through an aqueous solution of iodin until the latter is decolorized:

$$\underset{\text{Hydrogen sulphid.}}{H_2S} + I_2 = \underset{\text{Hydriodic acid.}}{2HI} + S.$$

If allowed to stand in the air, the colorless acid becomes oxidized, turns brown, and eventually disappears, while crystals of free iodin form.

$$4HI + O_2 = 2H_2O + 2I_2.$$

Syrupus acidi hydriodici (U. S. P.) contains 1 per cent. absolute HI. Dose: 30 to 60 ♏ (1.90–3.80 c.c.). It is unstable.

Acidum hydriodicum dilutum (U. S. P.) is a 10 per cent. aqueous solution of HI made by the action of tartaric acid, potassium iodid, and hypophosphite. It is not so stable as the syrup.

Oxyacids.—The effect of mixing iodin with caustic soda corresponds to that of mixing chlorin with the same hydroxid. First, the hypoiodite, NaIO, is formed; in a short while this changes to sodium iodate, $NaIO_3$, and sodium iodid, NaI. The acid from which the iodate is derived is iodic acid, HIO_3.

Iodic acid is a very stable, white crystalline substance, soluble in water and imparting to it the properties of a strong acid. It is odorless and has a bitter taste. It is used as a test for morphin, as it yields its oxygen readily and is thus reduced to brown elementary iodin.

Periodic acid, HIO_4, is formed when sodium iodate is oxidized by the action of chlorin. Taking up 1 atom more of oxygen, sodium periodate is produced. From this salt the acid can be obtained as colorless crystals, soluble in water and decomposable by heat. In this form it has 2 molecules of water combined with it, giving a formula H_5IO_6.

FLUORIN

Symbol, F. Atomic weight, 19.05.

Occurrence.—In nature fluorin exists in large quantities as *fluorspar*, calcium fluorid, CaF_2, and in *cryolite*, a fluorid of aluminium and sodium, Na_3AlF_6. Like the other halogens, fluorin is not found free in nature, owing to its active affinities for many substances.

Preparation.—When anhydrous hydrogen fluorid is converted into a conductor by dissolving in it calcium fluorid, the hydrogen fluorid is decomposed by the electric current, with fluorin separating at the anode. Vessels of platinum or copper resist the fluorin fairly well and are used instead of glass.

Properties.—Fluorin is an almost colorless, faintly yellow gas with a specific gravity of 1.265. It is condensed to a liquid at $-187°$ C. ($-304°$ F.). It combines with every element except oxygen and the argon family, and generally with great energy. All sorts of hydrogen compounds yield their hydrogen to it, with the evolution of light and heat.

Hydrogen Fluorid (HF).—This gas is prepared by gently heating in a lead dish a mixture of calcium fluorid and sulphuric acid. If it be covered with a glass plate the glass is corroded wherever it is exposed. By previously coating the glass with wax or paraffin and scratching with a needle through the wax the glass may be etched in ruled lines or ornamental figures. In this experiment aqueous vapor mixes with the gas. When absolutely dry the gas does not act on glass. The reaction is as follows:

$$\underset{\text{Calcium fluorid.}}{CaF_2} + H_2SO_4 = 2HF + \underset{\text{Calcium sulphate.}}{CaSO_4}$$

Hydrofluoric Acid.—The gas dissolved in water becomes a fuming liquid, which can not be kept in glass. Gutta-percha bottles, however, resist the action of the acid and are used as containers. The reaction with glass is shown in the following equation to be a conversion of the silicic acid into a gas, silicon fluorid:

$$\underset{\text{Silicic acid.}}{SiO_2} + \underset{\text{Hydrofluoric acid.}}{4HF} = 2H_2O + \underset{\text{Silicon fluorid.}}{SiF_4}$$

Toxicology.—Like hydrogen chlorid, this gas is highly irritating when inhaled, and the liquid acid corrodes the parts with

which it comes in contact. The antidote, when inhaled, is ammonia vapor; or, on the burned surfaces, weak alkalies to neutralize the acid.

Sodium fluorid is sometimes added to beer as a preservative. The amount in a single bottle has no noticeable effect, but if the preserved beer is taken habitually as a beverage the effects accumulate. They are seen in the neuralgias, weak heart, dropsies, phlebitis, painful urination, and loss of calcium salts from the system, impairing nutrition of the bones.

THE CHLORIN FAMILY OR HALOGENS

In a former section a list of the elements was given (see p. 117), arranged, according to a natural system, by their numeric progression in valence and atomic weights. This system was based upon the observation that in many cases elements that resemble one another could be grouped in triplets, the middle member of which was not only intermediate in properties, but also had an atomic weight very nearly the mean of two extremes. Thus, in the order of atomic weights, Cl=35.45, Br=79.92, I=126.92, the mean is 81.19.

$$\frac{35.46 \ + \ 126.92}{2} = 81.19.$$

Other examples are P=31, As=74.96, Sb=120, the mean 75.5. The calcium group: Ca = 40, Sr = 87.6, Ba = 137, the mean is 88.5.

The similarities of the chlorin group with the gradation in properties according to the atomic weights are shown in the following summary: They are all univalent, all volatile, and all form colored gases that are pungent and irritating. At room temperature Cl is a gas, Br is a liquid, I a solid. Their boiling-points rise in the same order with their specific gravities. In their chemical conduct and their bleaching and disinfectant powers Cl has the strongest affinities, Br next, and I last; thus illustrating a general principle, that in such a group the energy is inversely as the atomic weight. The lighter halogen always displaces the heavier from its salts, *i. e.*, the lighter forms ions; the heavier, elementary molecules. The tendency to ion formation is great in fluorin but very slight in iodin. The activity and stability of their hydrogen acids follow the same law, but the order for the oxygen acids is reversed. As for solubility in water, Cl is readily soluble, Br moderately, I feebly. Their salts with metals (called *haloid*) crystallize in cubes and are among the best germicides known. These elements are called *halogens* (*hals*, sea-salt) because they are generated from the sea: Cl from sea-water, Br

from sea-salt, I from seaweed. Fluorin is classed with the halogens, though there is a wider step from it to chlorin than there is between the other members of the series. It resembles the members of this group, however, more than it does those of any other.

Facts like those just stated might be adduced from other groups, all going to justify the empiric law formulated by Mendelejeff, that *the properties of the elements are a periodic function of their atomic weights* (p. 116). These relationships are recognized as pointing to the conclusion that in the closely allied elements of a group there is a common constituent. A more sweeping generalization is that all the elements are species or variations of one primal stuff. They are unmistakably akin, hence they probably have one common ancestry.

SULPHUR (Brimstone)

Symbol, S. Atomic weight, 32.07.

Occurrence.—In volcanic regions, especially those of Sicily, this element is found free and almost pure. In considerable amounts it is found in its natural compounds, the *blendes*, *glances*, *pyrites*, and *galena*, in the hydrogen sulphid of sulphur waters, and the protein of plants and animals.

Preparation.—Native sulphur is melted by setting fire to it, and while liquid it is run off from the unfused minerals associated with it into cylindric molds. In this form it is called *crude brimstone*. It is refined by distillation or sublimation and condensation. The vapor, received into a cool chamber, is deposited, first, as small crystals, making the yellow powder known as *flowers of sulphur*. As the chamber warms, the sulphur condenses into a liquid at the bottom and is drawn off into molds to make *roll sulphur*.

Physical Properties.—The native element is found as elongated octahedral crystals of a honey-yellow color, with a very faint taste and odor. Pure sulphur may fail to answer to the odor test, but if a small piece be laid on polished silver it gives off sufficient vapor in a few days to make a brown halo of silver sulphid. The effect on the silver accumulates by time until it is perceptible, while that on the sense of smell is necessarily transient, and not intensified by time. It is insoluble in water, but soluble in hot alcohol, chloroform, ether, carbon bisulphid, oils, and alkaline solutions. It melts at 114° C. (237.2° F.) to a thin straw-colored liquid, which becomes thick and brown, like molasses, as the heat rises to 160° C. (320° F.); at 250° C. (482° F.) it becomes dark red and viscid; gets thin and yellowish again at 340° C. (642° F.), until it reaches 440° C. (824° F.), when it boils, emitting a brownish vapor. These phenomena are remarkable excep-

tions to the rule that fluids become more mobile as the internal friction is lessened by the rise of temperature. On cooling, the hot sulphur passes through the same stages in the reverse order, solidifying as prismatic crystals.

Heat has a peculiar effect in changing the vapor density of this element, and, as the molecular weight is twice the vapor density, we can calculate the changes as variations in the mass of the molecule. These variations are due apparently to varying mixtures of two allotropic forms of the element in the state of vapor, in one of which there are two atoms to the molecule S_2 and the other eight atoms S_8. The 8-atom molecule, S_8, at 440° C. (824° F.) dissociates at 1000° C. (1832° F.) into 4 diatomic molecules $4(S_2)$.

Amorphous Sulphur.—If the dark brown melted sulphur at or above 250° C. (482° F.) be suddenly cooled by pouring it into cold water, it becomes a soft tenacious mass similar to elastic rubber. This condition is not permanent, for in some hours it changes into an opaque brittle mass of rhombic octahedra. If crystallization occurs at temperatures above 100° C. (212° F.), the sulphur forms oblique prisms, in no way resembling the octahedra. Sulphur exists then in two crystalline, and one amorphous, varieties.

Prismatic or Monoclinic Sulphur.—This is formed after fusion and is an amber yellow, having a specific gravity of 1.95, and melting at 120° C. (248° F.).

Rhombic octahedral sulphur is found in nature and results when sulphur is deposited from solution in carbon bisulphid. It has a specific gravity of 2.05 and melts at 114.5° C. (238° F.). On exposure to the air for several days each monoclinic prism ceases to be transparent and splits into octahedra.

Official Preparations.—*Sulphur sublimatum*, or *flowers of sulphur*, deposited from subliming the crude element, is an impure preparation used externally in medicine. *Sulphur lotum* is sulphur washed in water to free it of some of the sulphuric acid generated during sublimation. *Sulphur præcipitatum*, *lac sulphuris*, *milk of sulphur*, is a white powder so finely divided that the yellow color is lost. It is prepared by dissolving sulphur in water by means of lime, and precipitating with hydrochloric acid. It is the most active form for medicinal use. Dose: ½ to 2 dr. *Unguentum sulphuris* is a 15 per cent. ointment used as a parasiticide in skin diseases.

Chemical Properties.—Sulphur, when heated, takes fire, burning with a pale-blue flame and forming sulphur dioxid. As a component of gunpowder it generates the same gas. It burns in hydrogen, forming H_2S. Like oxygen, it is at times divalent and can

replace that element to generate compounds resembling those of oxygen. To indicate this the prefix *thio-* is used before the name of the oxygen compound. Thus, HOCN is cyanic acid and HSCN is *thiocyanic acid.*

Crystallography.—A solution of sodium chlorid, like that of most solids, when evaporated to a thick fluid and set aside, crystallizes—that is, the molecules of the solid separate in regular geometric form. The same phenomenon is observed when vapors of iodin, arsenic trioxid or other substances solidify. A body is called a *crystal* when it has many sides or plane surfaces, more or less symmetric, intersecting at definite angles. That there is an internal structure is shown by a tendency to break with planes of cleavage corresponding to the external surface planes. A well-known example is mica. Crystals transmit heat, light, and electricity differently in different directions, owing to this peculiar arrangement of their deep-seated parts. Perfect crystals are rare, because the conditions are seldom ideal. Before the shape is symmetrically developed another crystal may separate which is superimposed and, therefore, impedes the growth of the first formed. Still, as the angles are well defined and the relationship of the faces preserved, these constants are sufficient data for geometry to construct the ideal form of the crystal. There are substances, like gum, resin, and glass, which never show geometric structure, and are, therefore, called *amorphous*, or formless. These do not break in planes of cleavage, but conduct heat and electricity and transmit light equally well in all directions.

The crystalline form is a very definite property which forces itself upon our observation and is as characteristic as the points of freezing and boiling. It is a valuable means of identification, and is, therefore, classed among the significant characters of a substance.

The manifold external shapes of crystals can all be referred to one of six systems characterized by their imaginary axes and planes of symmetry.

1. The **regular system** includes crystals with three equal imaginary axes crossing in the center at right angles to each other. The simplest form is the *cube* (Fig. 42) with the axes terminating in the center of the surfaces. (Examples: sodium chlorid and other haloid salts.) If the solid angles of the cube be cut off, the law of its symmetry is preserved and a secondary form appears, the *right octahedron* (Fig. 45). (Examples: diamond, alum, arsenic trioxid.) By cutting off the edges of the octahedron and cube symmetrically the third derivative is obtained, the *rhombic dodecahedron* (Fig. 43). (Example: garnet.) The regular *tetrahedron* (Fig. 44) is obtained by cutting off the alternate solid angles of the

cube or extending the alternate faces of the octahedron (Fig. 44). (Example: boracite.)

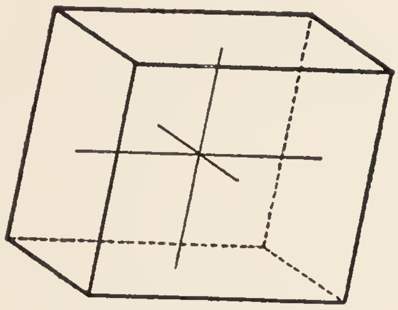


FIG. 42.—Cube.

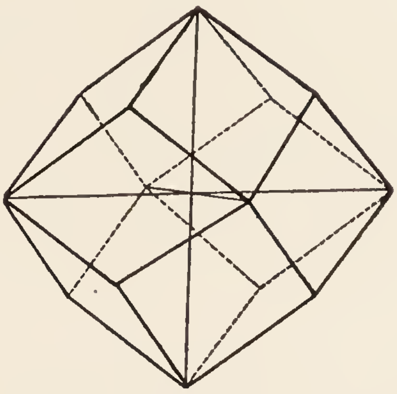


FIG. 43.—Dodecahedron.

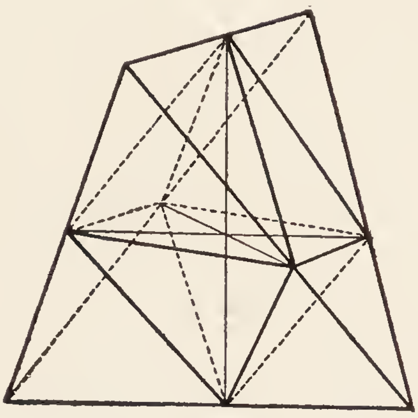


FIG. 44.—Tetrahedron developed from octahedron.

2. The **quadratic system** includes crystals with three axes intersecting at right angles, two of which are of equal length, the third differing and being called the principal axis. The simple forms are the *right square-based octahedron* (Fig. 45) and the *right-square prism* with a terminal plane at right angles to the principal

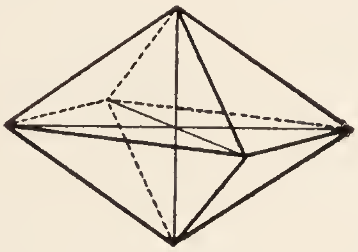


FIG. 45.—Quadratic octahedron.

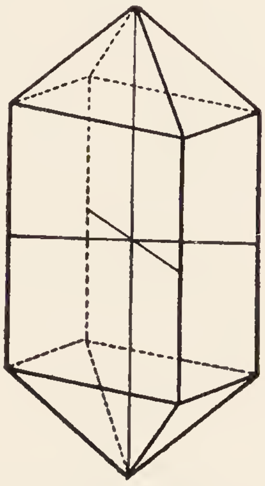


FIG. 46.—Quadratic prism with pyramidal end.

axis, or with terminal pyramids (Fig. 46). (Example: potassium ferrocyanid.)

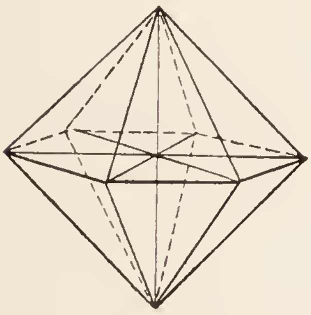


FIG. 47.—Double six-sided pyramid.

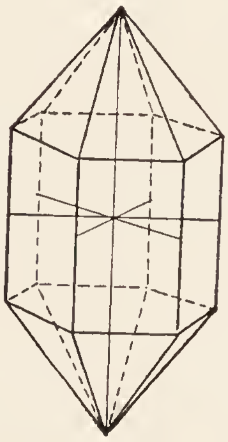


FIG. 48.—Hexagonal prism.

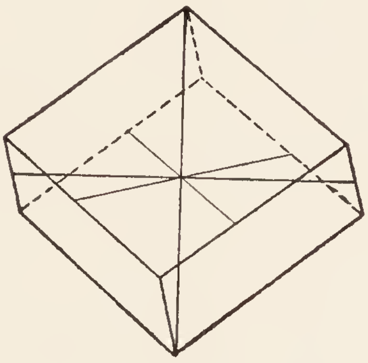


FIG. 49.—Rhombohedron.

3. The **hexagonal system** contains the forms referred to four axes, three of equal length, inclined to 60° to each other, and the fourth, of any length, at right angles to the other three. The fundamental form is the *double six-sided pyramid* (Fig. 47).

Another form is the *hexagonal prism* which, combined with the pyramids, gives the shape of the quartz crystal (Fig. 48). By developing the alternate faces of the double pyramid the *rhombohedron* is formed (Fig. 49), as in calcite or Iceland spar. (Example: ice.)

4. The **orthorhombic system** includes crystals that have three axes of unequal length intersecting at right angles to each other. The principal forms are the *right octahedron* or *double four-sided pyramid with rhombic base* (Fig. 51) and the *right rhombic prism.* (Examples: native sulphur and niter.)

5. The **monoclinic** and **oblique system** contains the crystals that can be referred to three axes, of equal or unequal length, two of them at acute angles, and the third at right angles to the other two. The fundamental form is a *double pyramid with an inclined axis* and a *rhombic base* (Fig. 50). Examples: sulphur from fusion, ferrous sulphate, sodium carbonate, cane-sugar.)

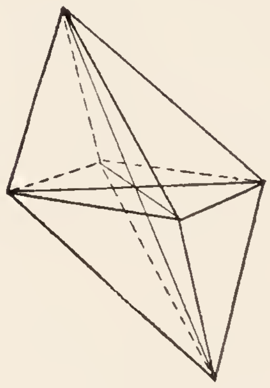


Fig. 50.—Monoclinic octahedron.

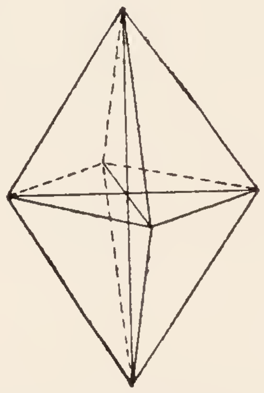


Fig. 51.—Orthorhombic octahedron.

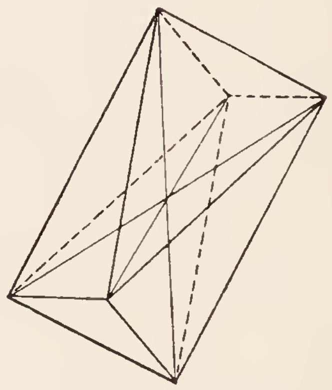


Fig. 52.—Triclinic octahedron.

6. The **triclinic system** groups together the crystals which can be referred to three axes, all inclined to one another at angles, not right angles. These crystals are the least symmetric, for only the parallel and opposite faces are equal, as in the *doubly oblique octahedron* (Fig. 52). (Examples: potassium bichromate, copper sulphate.)

When a substance has two definite forms, like sulphur, it is said to be *dimorphous.* These forms are found to differ in their specific gravities and other properties. Very rarely instances occur of the same substance forming crystals referable to three different systems; such substances are said to be *trimorphous.* There are many substances of different composition which crystallize in the same forms, and hence are said to be *isomorphous.* Among these there often exists a certain correspondence in the constitution of the molecules, as in the class of salts of different metals known as *alums*, so-called from their resemblance to the type, common alum.

Hydrogen Sulphid (H_2S) (*Sulphydric Acid, Sulphureted*

Hydrogen).—**Occurrence.**—Mineral springs of the class known as sulphur waters contain this gas. It is a product of the putrefactive fermentation of proteid substances, and hence is found in foul abscesses and in small amounts in the flatus of the intestines.

Preparation.—The most convenient method of preparation, and the one generally used, is that consisting in the action of dilute sulphuric acid on ferrous sulphid. Hydrochloric acid and antimony sulphid may also be used. In coarse pieces the ferrous sulphid is put into the usual hydrogen-generating flask (Fig. 28) and sulphuric or hydrochloric acid in the proportion of 1 : 6 of water is added as required. A wash-bottle containing water is attached to remove impurities. Kipp's apparatus (Fig. 53) is a convenient

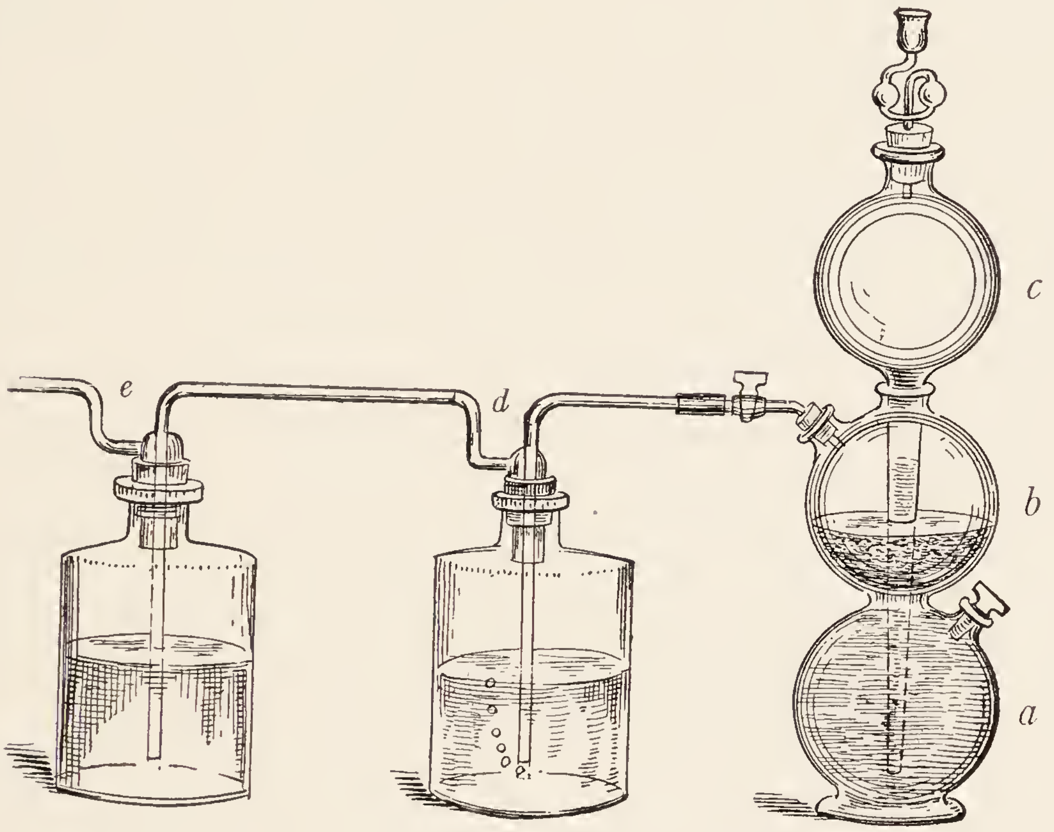


FIG. 53.—Kipp's apparatus for hydrogen sulphid, with wash-bottles attached.

source of the gas in a regulated supply. It has three vessels superposed; in *a* is the dilute sulphuric acid which is fed from *c*. It rises until it acts on the ferrous sulphid in the generator *b;* the gas confined presses out the acid, which then rises to *c*, and action ceases until the gas is allowed to escape at the cock, when the acid descends to its first position. The gas is washed in *d*, and acts on the metallic solution in *e*.

FeS	+	H_2SO_4	=	$FeSO_4$	+	H_2S
Ferrous sulphid.		Sulphuric acid.		Ferrous sulphate.		Hydrogen sulphid.
FeS	+	$2HCl$	=	$FeCl_2$	+	H_2S.
				Ferrous chlorid.		

Physical Properties.—Hydrogen sulphid is a gas without color, but having the disgusting odor and taste of rotten eggs. It is

slightly heavier than the air; specific gravity 1.19. At -74° C. (-101.2° F) it liquefies, and at -85.5° C. (-122° F.) it freezes into white crystals. One volume of water absorbs three of this gas at 20° C. to form a colorless solution having the odor and chemical powers of the gas itself. This is H_2S water. On boiling, all the gas is expelled. While this solution is useful in the laboratory, it is not stable, soon taking oxygen from the air to form water with the deposit of sulphur. To prevent this deterioration the water should first be boiled to expel the dissolved oxygen, and the solution then kept in well-filled and well-stoppered bottles. This solution is sometimes called *sulphydric acid.* With ammonia it forms two compounds, ammonium sulphid, $(NH_4)_2S$, and ammonium hydrosulphid, NH_4HS.

Chemical Properties.—If delivered at a jet, hydrogen sulphid burns with a blue flame, forming sulphur dioxid and water:

$$H_2S + 3O = SO_2 + H_2O.$$

An explosive mixture results when air is added to hydrogen sulphid. Soluble sulphydrates or hydrosulphids are produced by passing it into a solution of an alkaline hydroxid:

$$\underset{\text{Potassium hydroxid.}}{KOH} + H_2S = H_2O + \underset{\text{Potassium hydrosulphid.}}{KHS}.$$

As a Group Reagent.—Solutions of the heavy metals (p. 210), when charged with hydrogen sulphid yield sulphids and the acid of the salt is set free:

$$\underset{\text{Copper sulphate.}}{CuSO_4} + H_2S = \underset{\text{Copper sulphid.}}{CuS} + \underset{\text{Sulphuric acid.}}{H_2SO_4}.$$

The copper sulphid is thrown down as a brownish-black precipitate. With zinc sulphate a scanty white precipitate of zinc sulphid is produced according to the equation:

$$ZnSO_4 + H_2S = ZnS + H_2SO_4.$$

Even with excess of H_2S all the zinc is not precipitated, but some of its sulphid remains in solution. The addition of potassium hydroxid by removing the free H_2SO_4, causes a further precipitate of ZnS. If this ZnS be collected on a filter and treated in a test-tube with sulphuric acid, H_2S is liberated by a reaction, the reverse of that given above. This reversible character is shown in the equation

$$ZnS + H_2SO_4 \rightleftarrows ZnSO_4 + H_2S.$$

The different metallic sulphids behave differently to weak acids: When insoluble in acids (as is the case with sulphids of Pb, Bi, Ag, Hg, Cu, Cd, As, Sb, Au, Pt, Sn) there is a precipitate with hydrogen sulphid; when soluble in the acids (as is the case with sulphids of Fe, Co, Ni, Mn, Zn, Th, Ur) an alkali solution with the hydrogen sulphid precipitates them. This latter class is more conveniently precipitated by adding an alkaline sulphid or ammonium sulphid:

$$\underset{\text{Zinc chlorid.}}{ZnCl_2} + \underset{\text{Ammonium sulphid.}}{(NH_4)_2S} = \underset{\text{Zinc sulphid.}}{ZnS} + \underset{\text{Ammonium chlorid.}}{2NH_4Cl}$$

The metals of the alkalies and alkaline earths form with hydrogen sulphid soluble sulphids and make the analytic group of metals not precipitated by hydrogen sulphid or by ammonium sulphid.

Sulphur Cycle.—In the protein of plants and animals sulphur is essential to life. The plant gets its supply from the sulphates of the soil. The animal appropriates the plant protein as food, and both in decay give up the sulphur as H_2S, which in the air and soil is oxidized back to the sulphates of the circuit. These chemical reactions are facilitated by the soil-bacterial enzyms of reduction and oxidation (p. 546).

Toxicology.—If inhaled pure, this gas is immediately fatal, and even when diluted to 1 per cent. it kills, though more slowly. As a constituent of the gas of privies, burial vaults, sewers, and the slag heaps of chemical works its minor toxic symptoms are often seen. They are nausea, vomiting, depression, giddiness, headache, labored breathing, stupor, and coma. In laboratories it should not be used outside the fume chamber. The air contaminated with it acts as an insidious poison, partly by its power of reducing the hemoglobin of the blood-corpuscles, but mainly as a direct paralyzer of the nerve centers of the lungs and heart.

Postmortem Appearances.—The blood is liquid and dark brown in color, from the sulphid of iron formed with the red coloring-matter. A silver coin inserted into an incision blackens, even before putrefaction sets in.

Treatment consists in prompt removal to pure air, artificial respiration, inhalations of oxygen, warmth to the extremities, and stimulants.

Detection.—The odor is perceptible when 1 part is present in 10,000 of air. This may be confirmed by exposing a piece of white filter-paper soaked in solution of lead acetate; it blackens.

Sulphur Dioxid (SO_2) (*Sulphurous Anhydrid*).—**Preparation.**—When sulphur is burned in oxygen or in the air, direct union occurs: $S + O_2 = SO_2$. This method for the generation of sulphur dioxid is used for the disinfection of rooms. Sulphur dioxid is formed when certain sulphids, like pyrites, FeS_2, are roasted in

the air, as in the first step in the manufacture of sulphuric acid. One method of extemporaneous generation without heat convenient for the laboratory is to have on hand a solution of sodium bisulphite made from that salt or prepared by charging a solution of sodium carbonate with sulphur dioxid. This solution is placed in a tap-funnel of the apparatus Fig. 37. In the flask is concentrated sulphuric acid. On opening the cock, the bisulphite solution drops into the acid and SO_2 is set free at any desired rate.

$$\underset{\text{Sodium bisulphite.}}{NaHSO_3} + H_2SO_4 = \underset{\text{Sodium bisulphate.}}{NaHSO_4} + H_2O + SO_2.$$

The usual laboratory method is by heating strong sulphuric acid with copper in a flask seen in Fig. 41: $2H_2SO_4 + Cu = CuSO_4 + 2H_2O + SO_2$. Owing to its solubility in water the pneumatic trough is not used, but the gas is collected in upright jars with glass stoppers greased with vaselin.

Physical Properties.—Sulphur dioxid is a colorless gas with a stifling odor and a persistent taste, familiar in the odor and taste of the smoke of sulphur matches. Its specific gravity is 2.23; hence, it may be collected by downward displacement. At room temperature it is readily liquefied under three atmospheres of pressure, or under ordinary pressure if cooled artificially by a mixture of ice and salt to $-10°$ C. (14° F.). It freezes at $-75°$ C. ($-103°$ F.). Compressed in siphons, sealed cans, or steel cylinders it is a market product.

Chemical Properties.—Sulphur dioxid does not burn nor will it support combustion. If a handful of flowers of sulphur be thrown down a burning chimney the fire will be extinguished. The sulphur takes fire and yields SO_2, which smothers the flames. When SO_2 is passed into solutions of metallic hydroxids it forms sulphites or bisulphites, according to the amount of hydrogen replaced.

Acidum Sulphurosum.—Water dissolves about 50 times its volume of the gas at ordinary temperatures, resulting in the official *sulphurous acid*, H_2SO_3 (Fig. 41). After a bottle is filled with gas if a little water be added and the bottle closed and shaken, on opening again the air rushes in to take the place of the gas absorbed by the water. A test-tube filled with dry SO_2 and inverted with the mouth under water slowly fills with water. It is a colorless liquid with an acid reaction first reddening litmus and afterward bleaching it, and forms two classes of salts represented by sodium sulphite, Na_2SO_3, in which sulphosion $(SO_3)^{=}$ is divalent, and sodium bisulphite, $NaHSO_3$, containing univalent hydrosulphosion $(HSO_3)^{-}$. It is a weak acid, decomposing by heat into $H_2O + SO_2$. Sunlight causes rapid deterioration by oxidation.

The moist gas and even more, the acid solution, are characterized by their readiness to take one more atom of oxygen from substances rich in that element. They are, therefore, called powerful *reducing agents*, being converted themselves into a higher oxygen compound, sulphuric acid:

$$SO_2 + H_2O + O = H_2SO_4.$$

A striking exhibition of this reducing property is seen when the purple solution of potassium permanganate is added to sulphurous acid. The color is discharged, due to the yielding of oxygen to the H_2SO_3, which becomes H_2SO_4. Sulphur dioxid is also a bleaching agent, taking oxygen from vegetable dyes. This may be shown by burning sulphur near moist flowers under a bell jar. The flowers lose their color, which, however, can be partly restored by immersion in weak sulphuric acid.

With powerful reducing agents the gas may give up its oxygen, thus becoming an oxidizing agent:

$$4SO_2 + \underset{\text{Hydrogen sulphid.}}{3H_2S} = 2H_2O + \underset{\text{Pentathionic acid.}}{H_2S_5O_6} + S_2.$$

Medical Uses.—Sulphur dioxid is very destructive to plant life, high and low. A few pounds of sulphur burned in a mouldy cellar or conservatory causes the minute fungi to disappear. This property makes it valuable as an aërial disinfectant and vermin-killer. For every 1000 cu. ft. 4 pounds of sulphur must be burned. The sulphur candle may be used, or a mixture of flowers of sulphur and turpentine may be fired, if supported by bricks in a washtub containing water. As the gas is irrespirable, the combustion cannot be watched. The room must be kept tightly closed for twenty-four hours, and then aired before being occupied. All bugs, fleas, mosquitoes, and many bacteria are destroyed by this means. Many fabrics left in such an atmosphere are bleached, and perishable foods, such as meats and fruit, are made preservable for days. This preservative property is shared by its salts, the *sulphites* and bisulphites, which are often dusted over meats to prevent decay. Digestion of foods so preserved is retarded because the antiferments interfere with the activity of the enzymes of digestion. Sulphurous acid and the sulphites are prohibited by U. S. law (1908) as preservatives of food. Sulphur dioxid is not condemned when used in fumigating wines, dried fruits, or sugars to the extent of 350 mg. per kilogram left in the product. In these cases a certain amount combines with aldehyd and sugar to make harmless compounds, but any excess is toxic. *Acidum sulphurosum* is a parasiticide

for skin diseases. It is given internally to check gastric fermentations. Dose: f℥ss–j (2–4 c.c.), largely diluted.

Tests.—The stifling odor of burning sulphur matches is characteristic of sulphur dioxid. Starch-paper moistened with a solution of iodic acid turns blue when exposed to air containing 1 part of SO_2 in 3000.

Sulphur Trioxid (SO_3) (*Sulphuric Anhydrid*).—**Preparation.**—In burning sulphur most of it becomes SO_2, but a small quantity of misty substance is formed which has the formula SO_3. When fuming sulphuric acid is heated it decomposes with the production of SO_3.

$$\underset{\text{Pyrosulphuric acid.}}{H_2S_2O_7} = \underset{\text{Sulphuric acid.}}{H_2SO_4} + \underset{\text{Sulphur trioxid.}}{SO_3}.$$

Properties.—Sulphur trioxid is a transparent colorless liquid which freezes at 16° C. (60.8° F.) to a white solid. After being kept awhile a modified form is produced at ordinary temperature, forming white asbestos-like crystals. This white solid dissolves in water with a crackling sound, resulting in H_2SO_4 and evolving much heat. It is used by dyers as an oxidizing agent.

Sulphuric Acid (H_2SO_4) (*Oil of Vitriol*).—**Occurrence.**—In almost every technical process this acid is used at one stage or another. Its manufacture is of supreme importance in the arts, and illustrates some most interesting reactions.

Preparation.—Under the demand for sulphur trioxid in the manufacture of artificial indigo the *catalytic method* has been brought to a point of practical efficiency and economy. The theory is simplicity itself: By heating in the air ores of sulphur and iron (pyrites) SO_2 is formed. This is purified, cooled, and with the oxygen of the air passed through cylinders containing heated plates holding a mixture of finely divided platinum and asbestos. The SO_2 unites directly with O to form SO_3, which is dissolved in some weak sulphuric acid. It can be obtained of any desired strength from the ordinary sulphuric acid to the fuming article. Any arsenic in the SO_2 soon stops the action of the platinum; hence it is removed before the gas enters the cylinder. This insures a product which is arsenic free. As the platinum *does not enter into the reaction*, a small amount serves to oxidize very large quantities of the SO_2. It appears that a union which goes on very slowly between SO_2 and oxygen at all times is hastened to a high degree by *catalysis*, due to platinum, which facilitates the motion much as a lubricant does in machinery.

Lead-chamber Process.—This process can be illustrated simply by immersing in a vessel containing SO_2 a sliver of wood wet with nitric acid. Red fumes of N_2O_4 arise, which change to color-

less N_2O_2 when the vessel is closed. Again opening the vessel, air enters and N_2O_2 forms red fumes of N_2O_4. Eventually crystals of nitryl-sulphuric acid appear inside the glass and these are washed down with water to form impure H_2SO_4. The H_2SO_4 can be identified by evaporating with powdered sugar in a porcelain dish over a water-bath. The residue turns brown and then black. Until recently this was the most accepted method of manufacture. It is based on the principle of burning S to SO_2, mixing the gas with H_2O and O of the air, and accelerating their union by the aid of nitric acid and nitrogen oxid. Thus:

$$(1)\quad 2HNO_3 + SO_2 = H_2SO_4 + N_2O_4.$$

$$(2)\quad 2SO_2 + N_2O_4 = 2SO_3 + N_2O_2.$$

$$(3)\quad SO_3 + H_2O = H_2SO_4.$$

$$(4)\quad N_2O_2 + O_2 = N_2O_4.$$

These equations show how the nitrogen oxids act as go-betweens, taking up oxygen from the air and turning it over to the sulphur dioxid. The sulphur trioxid then joins with water to make sulphuric acid. The gases are mixed in a series of lead-lined chambers.

The lead lining resists the action of sulphuric acid until it gets to 80 per cent. acid. When further concentration is desired, this acid is evaporated in flat platinum stills.

Impurities of the crude acid are due, first, to the arsenic compounds volatilized from the roasting ore; second, to the lead sulphate formed in the chambers; third, to the nitro compounds still retained; fourth, to particles of straw and organic dust which give it a brownish color. The acid is purified by distillation.

Properties.—Pure, strong sulphuric acid (*acidum sulphuricum*, U. S.) of a specific gravity not below 1.826 contains not less than 92.5 per cent. of real acid (H_2SO_4), and is a colorless, heavy, oily liquid, not fuming, odorless, extremely sour, combining actively with water, and blackening or charring organic substances. It crystallizes at 10.5° C. (50.9° F.), and boils at 338° C. (640.4° F.). The commercial *oil of vitriol* is colored light brown by suspended carbonaceous matter and contains small amounts of dissolved metals, principally lead and arsenic. When added to water, heat is given out. If the proportion of the mixture be 3 of acid to 1 of water, the temperature will rise above 100° C. (212° F.). It has the property of abstracting water from the air, 100 gr. under favorable conditions absorbing 120 gr. of water in four days; hence its use in *desiccators* for drying precipitates on filter papers. One of the best methods of drying gases is by passing them through

concentrated sulphuric acid. This great affinity for water explains the charring action upon organic matter such as cane-sugar, paper, etc., from which it abstracts the elements of water while dissolving all but the black carbon. When the concentrated acid is heated with zinc, copper, or other metals, the gas sulphur dioxid is liberated; if the acid be dilute, then, if any action occurs, the gas evolved is hydrogen.

Nordhausen acid is a form manufactured in Bohemia and used largely in chemical industries. It is a dark-brown, heavy, oily, fuming liquid, with a specific gravity of 1.9. Its formula is $H_2S_2O_7$, and it is regarded by some as a solution of SO_3 in H_2SO_4. Two weaker forms are used in medicine, the dilute (*acidum sulphuricum dilutum*, U. S.), of 10 per cent. H_2SO_4, and the aromatic (*acidum sulphuricum aromaticum*, U. S.), of 20 per cent. H_2SO_4. Dose, 10 to 20 ♏ (0.66–1.23 c.c.).

Medical Uses.—The concentrated acid is applied externally as a powerful caustic in the shape of *Ricord's paste*, made with powdered charcoal, and *Michel's paste*, made with powdered asbestos.

The dilute forms only are used internally as solvents for quinin and as a remedy for night-sweats.

Its *incompatibles* are the alkalies; alcohol; salts of barium, calcium, strontium, lead, mercury, and silver; sulphids.

Monobasic and Dibasic Acids.—The halogen acids have but one combining weight or atom of hydrogen, as HCl, but the three sulphur acids already referred to, H_2S, H_2SO_3, and H_2SO_4, have two, both of which are replaceable by metals. With a bivalent metal, like calcium, but one salt is formed, by H_2SO_4; *i. e.*, $CaSO_4$, the calcium replacing both hydrogen atoms. As one or both of these hydrogen atoms may be replaced by a univalent metal, two different salts are conceivable. For example, with sodium there are two possible reactions:

$$H_2SO_4 + NaHO = NaHSO_4 + H_2O;$$

and

$$H_2SO_4 + 2NaHO = Na_2SO_4 + 2H_2O.$$

Acids, like hydrochloric, which have but one replaceable hydrogen atom and which, therefore, react with only one combining weight of a base to form but one salt, as NaCl, are called *monobasic*.

Acids, like sulphurous and sulphuric, which react either with one or with two combining weights of a base, are called *dibasic*. They have, as a rule, but two atoms of replaceable hydrogen, and when these are both replaced by a metal the salt is called *neutral* or *normal*. Salts of dibasic acids which have one atom of metal

retaining one of hydrogen, which is the characteristic component of acids, are called *acid* salts. Sometimes the two salts are designated by the prefixes *mono-* and *di-* to the name of the metal, as $NaHSO_4$, monosodium sulphate; Na_2SO_4, disodium sulphate. Again, they are called *primary* and *secondary*. Sometimes they are distinguished by calling the normal salt Na_2SO_4, sodium *sulphate;* and the acid salt $NaHSO_4$, *bisulphate.*

Dissociation of a Dibasic Acid.—Sulphuric acid forms two kinds of anions: (1) In concentrated solution the univalent hydrosulphanion $(HSO_4)^-$ predominates: $H_2SO_4 = H^+,(HSO_4)^-$; (2) when diluted this breaks down and dissociates into $2H^+$ and the bivalent sulphanion $(SO_4)^=$. When the dilution is sufficient there is complete dissociation: $H_2SO_4 = H^+,H^+,(SO_4)^=$. If an acid is *weak*, like carbonic acid, H_2CO_3, stage (1) prevails through all dilutions, the second hydrogen ion dissociating to only a slight degree. The solution of its acid salt, MHA (where M is any univalent metal and A a dibasic acid), forms the ions M^+ and $(HA)^-$, the group $(HA)^-$ scarcely breaking up at all. As there is little or no hydrion, there is a very slight acid reaction, and the so-called acid salt behaves like a neutral salt; it may even be alkaline in reaction, as is sodium bicarbonate, $NaHCO_3$. When the acid is *strong*, like sulphuric acid, dissociation is probably complete into H^+,H^+ and $A^=$. On dissolving its acid salt MHA the $(HA)^-$ at first formed undergoes further dissociation into the ions H^+ and $A^=$, and the solution finally contains the three ions, H^+, in relatively large amount, M^+, and $A^=$. The abundant hydrion gives it the properties of an acid.

Toxicology.—As there are few processes in the arts that do not use at some stage the oil of vitriol it can be had at any chemist's. It is used for cleansing metals as a household article. In countries where the law makes it difficult to purchase the arsenic or alkaloidal poisons the ease with which sulphuric acid can be procured makes it a very common poison in use by the poorer classes for suicidal purposes. It is rarely given in food for homicidal purposes, because it betrays the poisoner by the altered appearance of the charred food, by the stains on the clothing, lips, and tongue, by the fiery taste, and by the characteristic symptoms. It has been given to young children and even to adults in the form of medicine, taken, as disagreeable doses usually are, from a spoon back of the tongue, so as to avoid tasting.

Poisoning has occurred from the accidental substitution of sulphuric acid for oils, syrup, or glycerin. It has been poured into the ear, given by enema, and even injected into the vagina.

Local External Effects.—Malicious persons resort to sulphuric acid to disfigure the face or ruin the clothes by throwing a quantity

of it at the hated person. Occasionally in chemical laboratories, while experimenting with it, flasks containing it will burst and the contents be dashed into the face of the experimenter. If it strike the eye, blindness may result. In contact with the skin it causes great agony and a lasting scar. Instant action is necessary to prevent these serious effects. Water must be applied freely, the whole face immersed in a basin of it or held under a running tap, and the eyes opened under the water. A paste of sodium bicarbonate or a piece of soap will help to neutralize the residual acid at the burned points. The burn may be treated afterward with *linimentum calcis*. It is a common accident in the laboratory for the acid to fall upon the clothing. If not promptly touched with ammonia or some alkaline solution, the spot turns red and soon becomes rotten.

Symptoms.—On the instant of contact with the mouth there is intense pain, extending down the throat and gullet to the pit of the stomach, along the track of the acid. The tongue swells until it fills the mouth, and is covered with a white coating; later, it may be a corroded and shapeless mass.

The saliva flows profusely, but cannot be swallowed without pain, owing to the pharyngeal inflammation. Gasping and a hoarse voice denote that some of the acid has touched the larynx and caused spasmodic closure of the glottis.

The thirst is extreme, and is accompanied by persistent retching and vomiting. The ejected matter is very sour and slimy, often bloody, and loaded with portions of the mucous membrane of the gullet and stomach. The face has an agonized expression, the eyes look hollow, the nose is pinched and cold, the skin clammy, the pulse feeble, the breathing difficult, and the extremities are convulsed. The case may end fatally in a few hours or after several days by asphyxia, stupor, or convulsions. When perforation of the stomach is caused by rapid solution of its walls, the symptoms of fatal collapse rapidly develop and death is comparatively painless. When death is not so sudden, and the inflammatory symptoms subside, the unfortunate one has a lingering death of starvation from stricture of the gullet or of the pylorus, and an incurable dyspepsia due to destruction of the coats of the stomach.

Fatal Dose.—The smallest fatal dose reported as given to an adult is 60 gr. (3.8 gm.). Death ensued in a child of one year after 20 drops. It is difficult to state the minimum limit of fatality, owing to the fact that much depends on the part touched by the acid and much on the amount of food present in the stomach. Even the smallest amount would be permanently injurious if it reached the gullet, causing narrowing of the food channel. Few,

if any, infants survive this poison, and of the adult cases, the mortality is two-thirds.

Fatal Period.—In the infant quick inspiratory effort sometimes carries the poison into the larynx, and immediate death may ensue from spasmodic closure of the glottis. The shortest period recorded for the adult is one hour. Most cases die within twenty-four or thirty-six hours; some die from sequels after weeks, months, or years.

Treatment.—Three objects are to be kept in view: first, prompt neutralization of the acid; second, weakening by dilution; third, relief of the asphyxia, which sometimes threatens life immediately. For neutralization, magnesia and chalk are the best, but in an emergency soap-suds, whiting, or wall-plaster (an impure calcium carbonate) will serve the purpose. Weak alkaline solutions of sodium or potassium carbonate may be used with caution, as great distress, if not injury to the weakened walls, is possible from the stomach distention due to the liberation of large quantities of carbon dioxid gas. All the antidotes must be given suspended or dissolved in large quantities of water or milk. In the absence of a neutralizing antidote water alone must be used immediately and in large drafts, followed by raw eggs. Should symptoms of asphyxia appear as a result of laryngeal implication, then tracheotomy or intubation must be resorted to at once. Morphin may be given hypodermically to relieve pain, and nutritive enemata to support life. The sequels—perforation, collapse, contraction of the gullet, gastritis, and impaired digestion—must be treated by appropriate measures as the occasion requires.

Postmortem Appearances.—The *primary* pathologic changes found when death occurs within a few days are those of acute disorganization of the structures of the mouth, gullet, stomach, and neighboring parts. The lips and tongue are softened and eroded; the throat and gullet, whitish or gray in color, the first effect of the acid on mucous surfaces being to coat them with a white paint of altered secretion and membrane; the stomach is brown-red, due to imbibition of altered hematin, or black from charring, its mucous lining loose in shreds or patches, the folds large and deep from swelling, sometimes softened so as to tear under gentle manipulation; the peritoneum may be blackened from perforation; the duodenum red and thickened.

The *secondary* pathologic changes, seen when death follows after several weeks of chronic illness from some of the sequels, are ulceration of the gullet and contraction of its caliber from scars; the stomach is stripped of mucous membrane, partly or wholly red, its capacity much reduced by contraction, and its walls thickened and adherent to neighboring parts.

Tests.—*Acid Test.*—The free acid, in common with other acids, reddens litmus, turns cochineal yellow, and decolorizes red phenolphthalein.

Barium Chlorid Test.—It is customary to test for sulphuric acid and the soluble sulphates by first acidulating with hydrochloric acid to prevent a precipitate being produced by the salts of certain other acids, such as carbonic, phosphoric, and oxalic, and then adding a solution of barium chlorid, which throws down the white barium sulphate. Precipitation is hastened and perfected by boiling. This reaction occurs in the sense of the following equation:

$$\underset{\text{Ions.}}{H^+,H^+,(SO_4)^=} + \underset{\text{Ions.}}{Ba^{++},Cl^-,Cl^-} = \underset{\text{Ions.}}{2H^+,Cl^-} + \underset{\text{Molecules.}}{BaSO_4.}$$

As fast as the barium ions are neutralized by the sulphanion, the molecules of insoluble barium sulphate are formed and, not dissociating, are thrown down. This is in accordance with the principle: *If we mix solutions of acids, bases, and salts, any of whose ions are capable of uniting to form an insoluble compound, such compound is formed and precipitated.*

Charring Test.—When sulphuric acid is applied undiluted to white paper it darkens, and if gently heated chars the paper; even if largely diluted, by heating the paper so as not to scorch it, the water evaporates and the acid will reach the charring-point. In some degree this property is shared by hydrochloric acid.

Veratrin Test.—A drop of the free acid will turn the alkaloid veratrin yellow, and finally an unchanging crimson. When the free acid is very dilute, a fragment of veratrin is dissolved in it by the aid of heat, and the colorless solution, when evaporated to dryness in a water-bath, leaves a residue having a crimson edge, which persists after many hours.

Detection.—When the acid gets upon the clothing by accidental dropping, by expectoration, or by vomiting, detection is comparatively easy. The strong acid will leave upon black cloth a damp spot which is at first red and afterward dirty brown and rotten. If the cloth be colored with indigo-blue, there will be no red stain; if with logwood and madder, the stain will be yellow. The stain left by the dilute acid is also red, but the spot dries out and is not corroded. White linen or cotton will be blackened and eroded.

After many months or even years the acid may be detected in the spot by cutting out the piece, boiling it in 1 or 2 c.cm. (20–40 drops) of distilled water, filtering, and testing with barium chlorid. A control experiment should be conducted simultaneously with a piece of the unstained cloth. Woolen textures often naturally

contain sulphates, but if free sulphuric acid be present, the stain will turn blue litmus-paper red, will taste sour, and respond to the veratrin test. When some of the acid gets upon the lips, face, or hands, and is not instantly wiped or washed away, the burned spot does not blister, but turns brown, whereas with nitric acid it would stain yellow, and with muriatic acid there would be no stain whatever. The corroded skin soon sloughs, and the wound fills up by granulation, leaving a permanent scar.

While it is true that the free acid is very rarely found in the stomach after death and "the chemical detection of a poisoning by nitric or sulphuric acid is, as a rule, impossible," yet in the majority of cases detection is rendered sure by a study of the surroundings, the characteristic pathologic effects, and the stains. Sometimes it happens that these are not conclusive, and appeal must be taken to a *quantitative analysis*. The gastric secretions and the food always contain some sulphates; others, such as magnesium sulphate, may have been given as a medicine. It is, therefore, necessary to estimate the total quantity of sulphates present, and judge if the amount be greater than normal, and if it can be accounted for in any other way than by the administration of the acid itself. The mineral acids are usually separated from organic matter by digesting the mixture in distilled water for several hours. An acid reaction with litmus would point to free acid, and the degree of acidity could be determined by allowing the suspended matter to subside and then titrating a definite portion with decinormal sodium hydroxid, using phenolphthalein as an indicator. Some degree of acidity must be expected of the gastric contents from the presence of natural acids—hydrochloric, lactic, acetic, or butyric. The normal amount is so slight—not more than 0.3 per cent.—that any considerable showing of acid would be very significant.

To get the free sulphuric acid apart from free hydrochloric or butyric acids and separated from the sulphates and phosphates the watery extract above referred to should be evaporated to dryness and treated with a mixture of equal parts of alcohol and ether. This mixture will separate the free sulphuric and phosphoric acids and then by precipitation with acidified barium chlorid, boiling and weighing the dried precipitate of barium sulphate, the amount of free sulphuric acid can be ascertained. The total quantity of the free acid and that combined as sulphates may be calculated by precipitation with barium chlorid from a definite fraction of the liquid containing a small amount of hydrochloric acid and heated to boiling. The liquid should be decanted, the precipitate washed, collected on a filter, dried, and weighed. One hundred parts of the barium sulphate precipitated represent 42

parts of absolute sulphuric acid (H_2SO_4), or 34.3 parts of sulphuric anhydrid (SO_3). By comparing the result with the small amount of sulphuric acid ordinarily present in a mixed meal (not more than 0.6 gm. or 10 gr.), the fact of excess can be made out.

The tissues rarely show free sulphuric acid, owing to its reaction with the phosphates. It forms sulphates with the bases and liberates the phosphoric acid. If the extract made with alcohol and ether, as stated above, when treated with ammonium molybdate, should yield a yellow precipitate, this would be an indication that free sulphuric acid had been present, unless it could be shown that free phosphoric acid had been given.

As the proportion of sulphates normally present in the *urine* varies with the individual, and in the same person changes from day to day, no forensic importance is to be attached to the analysis of the urine.

Oxyacids of Sulphur.—The compounds of sulphur with oxygen and hydrogen are as follows:

Thiosulphuric acid, $H_2S_2O_3$,	Persulphuric acid, $H_2S_2O_8$,
Hydrosulphurous acid, $H_2S_2O_4$,	Dithionic acid, $H_2S_2O_6$
Sulphurous acid, H_2SO_3,	Trithionic acid, $H_2S_3O_6$,
Sulphuric acid, H_2SO_4,	Tetrathionic acid, $H_2S_4O_6$,
Pyrosulphuric acid, $H_2S_2O_7$,	Pentathionic acid, $H_2S_5O_6$.

The acids sulphurous, sulphuric, pyrosulphuric (Nordhausen), and thiosulphuric are of importance, but little is as yet known concerning the others.

Thiosulphuric Acid ($H_2S_2O_3$) (*Hyposulphurous*).—The anion of this acid is $(S_2O_3)^=$, which differs from the sulphuric ion $(SO_4)^=$ by having one oxygen replaced by one sulphur atom. This gives the name *thiosulphuric* from *thion*, the Greek for sulphur. It is commonly known only in a combination such as sodium hyposulphite (thiosulphate), $Na_2S_2O_3 + 5H_2O$, or potassium hyposulphite (thiosulphate), $K_2S_2O_3 + 5H_2O$. These salts have the power of dissolving the silver salts which have escaped the action of light, and are largely used, under the name *hypo*, for fixing the image in photography. Sodium hyposulphite is prepared by passing sulphur dioxid into a mixture of sodium sulphid and caustic soda. Thus:

$$2Na_2S + 2NaOH + 4SO_2 = H_2O + 3Na_2S_2O_3.$$

SELENIUM

Symbol, Se. Atomic weight, 79.2.

TELLURIUM

Symbol, Te. Atomic weight, 127.5.

Selenium is found associated with sulphur and, like it, has different allotropic forms. The amorphous variety is a black or dark-red solid which, kept at a temperature of 150° C., changes

to the crystalline variety, gray, and with a metallic luster. Its electric conductivity varies directly as the light it receives. Tellurium forms grayish-white crystals with a metallic luster occurring free in nature or as tellurid of gold and other metals. Both of these non-metals are very rare, being found in small quantities. Closely allied to sulphur they form anhydrids like SO_2 and SO_3, which, with water, form *-ous* and *-ic* acids, H_2SeO_3 and H_2SeO_4, and H_2TeO_3 and H_2TeO_4; analogous to H_2SO_3 and H_2SO_4. With hydrogen they form gases, H_2Se and H_2Te, which resemble H_2S in their mode of formation, their odor, and their reaction with metallic solutions, but which are less stable, with odors more disgusting than hydrogen sulphid. All of them on combustion yield dioxids.

Sulphur Group.—A trinity corresponding to the halogens is formed by sulphur, selenium, and tellurium. They are divalent and sometimes tetravalent, hexavalent, or octavalent. Their atomic weights are S., 32; Se., 79.2; Te., 127. The mean is 79.5, which is nearly the atomic weight of Se. Their properties are similar, but vary in the order of their atomic weight.

COMPOUNDS OF NITROGEN AND OXYGEN

Nitric Acid (HNO_3) (*Aqua Fortis*).—**Occurrence.**—Nitric acid is not free in nature. As the result of the oxidation of nitrogenous animal matter potassium and sodium nitrate are widely disseminated, especially in guano deposits. The nitrates are also to be found in traces in rain-water and in the surface wells of towns.

Preparation.—Either potassium or sodium nitrate will yield nitric acid when distilled with sulphuric acid. Though nitric acid is the stronger acid, yet, owing to its volatility, it gives place to sulphuric acid, which is non-volatile. This is according to a general law: that, *given the materials to form a volatile compound, it is always formed and passes off in vapor.*

$$\underset{\text{Sodium nitrate.}}{NaNO_3} + H_2SO_4 = \underset{\text{Monosodium sulphate.}}{NaHSO_4} + HNO_3.$$

Physical Properties.—Pure nitric acid is a colorless liquid, boiling at 86° C. (186.8° F.) and solidifying at −47° C. (−52.6° F.). The commercial article is yellow and of two different strengths: *single aqua fortis*, specific gravity 1.25, containing 39 per cent. of HNO_3, and *double aqua fortis*, specific gravity 1.4, with 64 per cent. of HNO_3. *Red fuming* nitric acid has a specific gravity 1.6 and is obtained by distilling at a high temperature or by adding reducing organic matter during distillation.

Chemical Properties.—Nitric acid takes rank with the strongest acids because it dissociates hydrion to a great degree. For

the same reason its conductivity as an electrolyte is high. It attacks and dissolves all the metals except gold and the platinum family. Its neutral salts, the nitrates, are all soluble in water. The compound formed with albumin is insoluble. Nitric acid does not keep pure long, the sunlight alone having power to decompose it into oxygen, water, and lower nitrogen oxids of a yellow color which dissolve in the water.

$$2HNO_3 = \underset{\text{Nitrogen tetroxid.}}{N_2O_4} + H_2O + O.$$

The strong tendency of nitric acid to form ions makes easy this production of water. The hydrion H^+, stimulated by sunlight, breaks up the anion $(NO_3)^-$ because it appropriates the oxygen ions forming undissociated water molecules. The velocity with which the oxidizing effect is produced is accelerated by the presence of N_2O_4 acting as a catalyzer. Hence for high oxidation effects the *red fuming* acid is preferred.

Most of the value of nitric acid, chemically, is due to this instability, which it shares with ozone and hydrogen dioxid. In the presence of substances that can be oxidized this power is exerted to a marked extent, red fumes of lower oxids arising. In its reaction with metals the hydrogen is not always liberated, but is taken up by the oxygen to form water, thus causing the formation of the reddish nitrous fumes. It is a monobasic acid dissociating as H^+, $(NO_3)^-$ and yielding but one class of salts, such as Na^+, $(NO_3)^-$.

Technical Uses.—Metal workers use this acid for etching and for cleansing preparatory to gilding and lacquering. Of late years it has had a great extension of employment in the making of various organic nitrocompounds, such as gun-cotton, celluloid, nitroglycerin, dynamite, and picric acid. Dyers, hatters, and chemists have need for it.

Medical Uses.—It is used in medicine as a valued caustic only under the official name *acidum nitricum*, of specific gravity 1.40, containing 68 per cent. HNO_3. On prolonged exposure to light and air the lower oxids of nitrogen are developed and impart a yellow color. It is then called *nitrosonitric* or *fuming acid*, useful as a reagent for biliary coloring matter in Gmelin's test. As an escharotic it corrodes organic matter by oxidation, not by carbonizing, as sulphuric acid does. Animal matter is turned a deep yellow, the color of picric acid. Albumin is coagulated by it, and if the acid be strong the white coagulum turns the characteristic yellow. It gives promptly the acid reaction with litmus and other color indicators. If concentrated it turns litmus yellow.

Acidum nitricum dilutum (U. S.), specific gravity 1.054, containing 10 per cent. HNO_3, is the only form suited for internal administration. The dose is 5–15 ♏ (0.33–1 c.c.), largely diluted.

Incompatibles.—Alkalies and alkaline earths and their carbonates, calomel, and other mercurous salts.

Toxicology.—Although widely used in the arts, this acid figures as a poison much less frequently than does sulphuric acid. History shows that most of the cases are suicidal, and when the intent is homicidal, the victim is either a child or an adult rendered unconscious by sleep or drunkenness. It would not be possible to give it in food or medicine without detection.

Symptoms.—There is no important difference from the symptoms produced by sulphuric acid and already described (p. 164), with the exception of the color of the mouth and lips, which, with nitric acid, is intensely yellow, though at first the parts are blanched and white. There are intense pain, vomiting, thirst, and great depression. Eructations of gas are frequent and distressing, due to its direct development by the action of the acid on organic substances.

Fatal Dose.—Three fluidrams by the mouth in adults have destroyed life, but a much smaller quantity would suffice to cause fatal suffocation from spasmodic closure if it were to enter the larynx, as it is likely to do in children.

Fatal Period.—The average duration of life is about twenty-four hours; the shortest time reported in the case of an adult was an hour and three-quarters, while a case is recorded of an infant who died in a few minutes. In some cases death has been delayed for weeks, months, or years, the remote effects of the poison then proving fatal.

Treatment.—The extraordinary energy and rapidity of action of nitric acid make it difficult to administer antidotes with sufficient promptness to be of much help. It is always advisable to use chalk, whiting, magnesia in milk, soapsuds, and eggs as antidotes, with the hope of neutralizing some free acid. The method is the same as for sulphuric acid and for the corrosive acids generally. In all there is instant local death of parts struck by the poison, rapidly followed by inflammation of surrounding viscera. Our antidotes cannot restore the tissues to health, nor can they diffuse into distant parts fast enough to be of much avail. The symptoms must be treated on general principles as they appear.

Postmortem Appearances.—All the parts to which the acid is applied present the various marks of erosion—in places hardening and thickening, in others ulceration and sloughing, general pulpiness, shreddy mucous surfaces denuded of membrane, and perforations of the gullet, the stomach, or the intestine. The

most characteristic pathologic change is the permanent citron-yellow or orange-brown color of the tissues acted on.

Tests.—Even when very largely diluted—that is, 0.2 per cent.—the acid reddens litmus (see Tests for Free Mineral Acids, p. 138).

Copper Test.—Poured upon slips of copper and gently heated, effervescence occurs and red-brown vapors arise that redden moist litmus-paper. If the amount of nitric acid be small, the color of the fumes may not be noticed, and a more delicate test is required. By holding in the vapors a piece of paper moistened with potassium iodid and starch paste a blue color develops.

Brucin Test.—Upon a crystal of brucin a drop of nitric acid strikes a blood-red color; upon morphin an orange hue, with orange-colored fumes.

Ferrous Sulphate Test.—Upon a white porcelain surface put a few drops of the suspected liquid, a drop of sulphuric acid, and a crystal of ferrous sulphate; the crystal turns dark-green, and finally brown. Even the combined acid in nitrates yields the same proof with any of the above tests, provided pure sulphuric acid is first used to free the nitric acid. If eggs have been given as an antidote, the nitric acid must be taken from the albumin by means of a solution of potassium carbonate; the resulting soluble nitrate can then be treated by equal parts of sulphuric acid and water before applying the above tests.

Detection.—On inspection the stains left on the clothing will be found dry and partaking of the same citron-yellow change found on the skin or other animal tissue touched by this acid. The yellow stain produced by tincture of iodin is discharged by potassium hydroxid or by ammonia-water, but the nitric-acid stain is indelible; ammonia and the alkalies only intensify it to an orange hue. If the piece of stained cloth be boiled in some distilled water, litmus-paper will reveal the acid reaction. When the acid liquid is neutralized with potassium carbonate, filtered and evaporated to dryness, crystals of potassium nitrate form. When these crystals are dissolved in water and a drop of pure sulphuric acid is added, the nitric acid is set free and strikes a blood-red color with brucin, yields ruddy fumes with copper turnings, or responds to the ferrous-sulphate test for nitric acid.

If the vomited matters be decidedly acid, the acidity should be measured by titration with decinormal solution of sodium hydroxid. The resulting sodium nitrate can then be tested by treating with sulphuric acid and applying any of the tests above mentioned.

As nitrates are not constituents of ordinary food or of the animal tissues, it is proof enough if these be found in any amount above a trace. It is not necessary to make a quantitative

analysis. The vomited matters or the tissues should be extracted with boiling distilled water and potassium carbonate and then filtered. Crystals of potassium nitrate are obtained on evaporation which respond to all the tests given above for nitrates.

Fumes of Nitric Acid.—The emanations of nitric acid are a mixture of nitric acid vapor with various lower oxids, all of them offensive and irritating to the air-passages. In the industries mentioned above as making use of this acid these vapors may do great harm if the processes be not carried on in closed vessels and the noxious fumes passed into milk of lime. The habitual breathing of air containing only a small amount frequently leads to severe chronic bronchitis with general impairment of health. In the annals of toxicology cases of acute poisoning are reported from chemists suddenly inhaling the fumes rising when a carboy of the acid has been accidentally broken. The symptoms are like those of capillary bronchitis.

In fatal cases there is found usually congestion of the larynx, trachea, and bronchial tubes, and sometimes edema of the lungs or effusion of blood. Although the effects appear to be mainly those of direct irritation, some cases show inflammatory changes in the lining of the right auricle. Acute cases should be treated by fresh air and inhalations of ether to relieve the sense of constriction.

Nitromuriatic Acid (*Acidum Nitrohydrochloricum*, U. S.).—By mixing 1 part of nitric and 3 parts of hydrochloric acid the commercial *aqua regia* is prepared. This is an unstable liquid, evolving free chlorin and other gases, and eventually becoming much weaker than when first made. The nitric acid oxidizes the hydrochloric, taking its hydrogen to form water and liberating chlorin and chloronitrous gas:

$$3HCl + HNO_3 = Cl_2 + NOCl + 2H_2O.$$

The nascent chlorin will act on gold and platinum, forming soluble chlorids. It dissolves all the metals, including gold and platinum, and oxidizes iodin, phosphorus, and sulphur. It coagulates albumin, turns it yellow, and finally dissolves it, as it does all vegetable and animal substances, with the production of ruddy fumes.

Acidum Nitrohydrochloricum Dilutum (U. S.).—Dose, 5–8 ♏ (0.30–0.50 c.c.). While the dilute acid is given internally as a medicine, the concentrated acid is an exceedingly corrosive poison, the symptoms and postmortem appearances of which differ from those of nitric acid in degree only. The antidotes are the same as for the other mineral acids.

NITROGEN OXIDS

In nature certain bacteria growing in nodules on the roots of leguminous plants have the power of uniting the nitrogen and oxygen of the air, enriching the soil with nitrates. By passing streams of electric sparks through the air an acrid smell is perceived and red vapors arise. These are nitrogen trioxid and tetroxid, and, when washed down with alkaline fluids, nitrites and nitrates are formed. In another place, as illustrating the law of multiple proportions, the following five compounds have been mentioned:

Nitrogen pentoxid, or nitric anhydrid	N_2O_5.
Nitrogen tetroxid, or dioxid	NO_2 or N_2O_4.
Nitrogen trioxid, or nitrous anhydrid	N_2O_3.
Nitric oxid	NO.
Nitrogen monoxid, nitrous oxid, or laughing gas	N_2O.

Nitrogen pentoxid, N_2O_5 (*anhydrous nitric acid*), can be prepared by removing water from 2 molecules of nitric acid, $H_2N_2O_6$, which then becomes N_2O_5. Nothing will serve but the most powerful dehydrating substance, phosphorus pentoxid, P_2O_5. The mixture distilled yields the nitric anhydrid as a white crystalline substance. This easily decomposes by reversing the process by which it was made, taking up the elements of water.

$$N_2O_5 + H_2O = H_2N_2O_6 \text{ or } 2HNO_3.$$

Nitric Oxid (NO).—By analytic methods it has been shown that a number of lower oxids, reduction products, are formed by the action of HNO_3 on copper or other metals. They vary according to the concentration of the acid, the nature of the metal, and the temperature. The one yielded most easily when copper clippings are used as the metal is the gas NO. The reaction is as follows:

$$3Cu + 8HNO_3 = \underset{\text{Copper nitrate.}}{3Cu(NO_3)_2} + \underset{\text{Nitric oxid.}}{2NO} + 4H_2O.$$

The first brown vapors are made colorless in passing through the pneumatic trough. This colorless gas, NO, is feebly soluble. It neither burns nor supports combustion. If collected in a bell jar and oxygen admitted, there is instant union, with the formation of reddish-brown nitrogen dioxid: $NO + O = NO_2$. This red gas is dissolved by the water which rises in the jar as the volume of the residual gas diminishes. Nitrogen dioxid is taken up by solution of ferrous sulphate, which turns dark brown (see Tests for Nitric Acid, p. 172).

Nitrogen Tetroxid (N_2O_4) (*Nitrogen Peroxid, Hyponitric Acid*).—The brown-red fumes formed by the union of NO with oxygen in the air can be condensed to a yellow liquid which loses color with an accompanying decline of temperature. It solidifies at $-12°$ C. ($-10.4°$ F.) into colorless crystals. A study of the vapor density shows that the dark-red gas at 100° C. (212° F.) has the formula NO_2, but the almost colorless gas

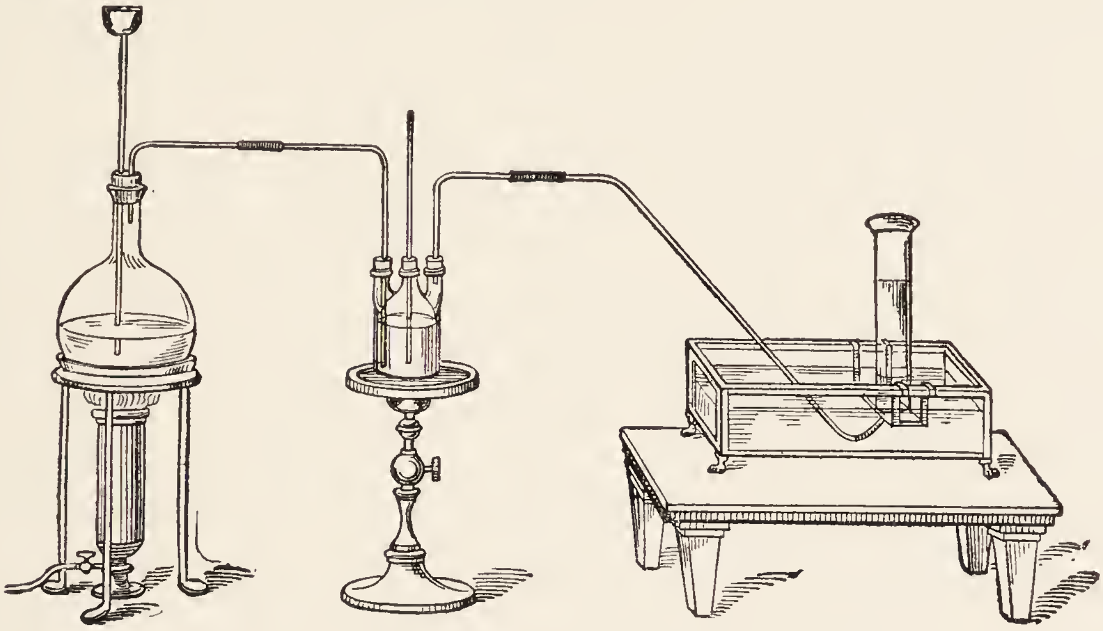


FIG. 54.—Apparatus for generating nitrogen dioxid.

below 0° C. (32° F.) has the formula N_2O_4 or $2(NO_2)$. At intermediate temperatures the gas is a mixture of the two forms. As stated above, it is the final product of electric discharges in the air, and dissolved in water it decomposes into nitric and nitrous acids.

$$N_2O_4 + H_2O = \underset{\text{Nitric acid.}}{HNO_3} + \underset{\text{Nitrous acid.}}{HNO_2}.$$

Toxicology.—In the manufacture of gun-cotton, oil of vitriol, oxalic acid, nitrobenzol, picric acid, and in metal working and gilding, the deoxidized nitric acid is the source of offensive, irritating, and, when very strong, deadly vapors, of which the chief constituent is nitrogen tetroxid. Workmen breathing it habitually suffer from chronic bronchitis with cough, suffocative attacks, dysuria, and delirium. These symptoms may culminate in death.

Nitrous Acid (HNO_2).—On reducing potassium nitrate with lead a salt is formed having less oxygen: potassium nitrite.

$$\underset{\text{Nitrate.}}{KNO_3} + Pb = \underset{\text{Nitrite.}}{KNO_2} + PbO.$$

The nitrite being soluble can be removed by water from the insoluble lead oxid. Again, by carefully heating KNO_3 it loses oxygen, yielding the nitrite:

$$2KNO_3 = O_2 + 2KNO_2.$$

The acid, as such, cannot be liberated from this salt by the action of sulphuric acid; it is too unstable at ordinary temperatures, but brownish vapors arise of *nitrogen trioxid*, N_2O_3, sometimes called *nitrous anhydrid*, which decomposes into NO_2+NO. It condenses to a dark indigo-blue liquid which boils at 0° C. (32° F.) and solidifies at −82° C. (−115.6° F.). This brown gas passed into water forms a blue solution containing some nitrous acid, but soon decomposes into nitrogen dioxid, nitric acid, and water.

$$\underset{\text{Nitrous acid.}}{3HNO_2} = 2NO + \underset{\text{Nitric acid.}}{HNO_3} + H_2O.$$

Tests for Nitrites.—Salts having the ion $(NO_2)'$ give the same brown reaction with ferrous sulphate as that referred to among the tests for nitric acid; but when treated with sulphuric acid the nitrites are peculiar in yielding the brown vapors of N_2O_3. Nitrites deoxidize and decolorize instantly the purple solution of potassium permanganate.

Nitrous oxid (N_2O) (*Nitrogen monoxid, "Laughing Gas"*).—**Preparation.**—By gradually heating ammonium nitrate to 250° C. (482° F.) in a retort the crystals melt and easily decompose, water being formed and a permanent gas generated, capable of being collected over hot water or mercury.

$$\underset{\text{Ammonium nitrate.}}{NH_4NO_3} = \underset{\text{Nitrous oxid.}}{N_2O} + 2H_2O.$$

To purify the product for inhalation the gas should be passed through warm solutions of sodium hydroxid and ferrous sulphate.

Properties.—Nitrous oxid is a colorless gas with a sweetish odor and taste; it is soluble in an equal volume of water and readily liquefied by pressure. The liquid is a useful refrigerating agent. Nitrous oxid does not burn, but yields oxygen to burning substances, supporting the combustion of carbon and phosphorus almost as well as oxygen. It does not part with its oxygen to burning sulphur when the flame is small, but with a large flame forms SO_2 just as would free oxygen. It does not break up and give oxygen to the body. Hemoglobin cannot use it.

Physiologic Effect.—Nitrous oxid gets the name *laughing gas* from the gay intoxication first caused by inhaling it mixed with air. When pushed beyond this hysteric stage or when inhaled pure the effects are those of a transient narcotic.

Toxicology.—As the organism does not have the power to utilize the oxygen in this gas when it is inhaled, along with anesthesia, some asphyxia is produced, which in healthy subjects can be borne long enough for short operations, such as tooth extraction. To prolong its effects with safety oxygen must be mixed

with it. Very rarely its administration has been fatal; some heart weakness is responsible for this result in most cases.

Hyponitrous Acid (HNO).—This substance can be obtained in white crystalline scales which readily explode, owing to their instability. Dissolved in water, it soon evolves the gas nitrogen monoxid, N_2O. Sodium hyponitrite is a permanent salt made by the reduction of sodium nitrite with metallic sodium in amalgam:

$$\underset{\text{Sodium nitrite.}}{NaNO_2} + 2Na + H_2O = \underset{\text{Sodium hyponitrite.}}{NaNO} + 2NaHO.$$

PHOSPHORUS

Symbol, P. Atomic weight, 31.

Occurrence.—This element is not found free in nature, occurring in combination mainly as phosphates in various minerals of the soil and in the structure of plants and animals. It was first discovered as a constituent of human urine.

Preparation.—Phosphorus is made from bone-ash, $Ca_3(PO_4)_2$, by heating it with carbon and sand in an electric furnace. This reduces the bone phosphate of calcium to elementary phosphorus, which is distilled and run into molds under warm water to make stick phosphorus.

$$\underset{\text{Calcium phosphate.}}{2Ca_3(PO_4)_2} + 10C + \underset{\text{Silicon dioxid.}}{6SiO_2} = 10CO + \underset{\text{Calcium silicate.}}{6CaSiO_3} + P_4.$$

Properties.—The *ordinary crystalline* or *waxy* form usually occurs in translucent cylinders which cut like wax, and when kept under water turn yellow and become coated with a thin white crust. As it oxidizes in the air it should be kept under water that has been well boiled to expel dissolved oxygen. It takes fire at 50° C. (122° F.), a temperature easily reached by friction between the fingers, hence the caution to handle it with forceps. If it should take fire in the hand, it will burn severely, and at the same time more or less of the poison will be absorbed. The poison in the burn should be made inert by a lotion of chlorinated soda or a paste of chlorinated lime.

It has the odor and taste of garlic, is very sparingly soluble in water, slightly soluble in alcohol and glycerin, but freely so in carbon bisulphid, almond oil, and ether. Under water at 44.5° C. (111° F.) it melts to an oily fluid, which can be run into cylindric molds. Exposed to the air, white fumes of its lower oxid, P_2O_3, are evolved, and in the dark emit a feeble light. *Black* and *white* phosphorus are modifications of no practical importance.

Red phosphorus is an allotropic form made by heating the waxy variety to 240° to 250° C. in a closed vessel without air for thirty-

six hours. It is a red-brown crystalline powder, insoluble in the solvents for waxy phosphorus, does not oxidize in air, is not luminous, need not be kept under water, and requires a much higher temperature to inflame it than does the waxy form. It does not take fire unless heated to 280° C. (536° F.). The pure red phosphorus is not poisonous, but the commercial article sometimes contains as much as 0.6 per cent. of the waxy, poisonous form.

The *lucifer matches* commonly sold are tipped with waxy or poisonous phosphorus mixed with potassium chlorate, sand, and glue, but the "*safety-match*" is tipped with potassium chlorate and antimony sulphid without phosphorus. In order to light the "safety-match" it must be rubbed upon the side of the containing box, which is covered with a thin coat of red or non-poisonous phosphorus, mixed with sizing.

There is some resemblance between nitrogen and phosphorus in their corresponding compounds with hydrogen, both forming gaseous compounds, NH_3 and PH_3; with oxygen, N_2O_3, N_2O_5 and P_2O_3, P_2O_5. Like nitric acid, HNO_3, there is a metaphosphoric acid, HPO_3.

The molecular weight of phosphorus is 124, which is four times the atomic weight, 31; hence there must be four atoms in its molecule.

Pharmaceutic Preparations.—In Pilulæ phosphori (U. S. P.) the pill mass is made with althæa and acacia, and each pill is coated with balsam tolu. The presence of the free phosphorus can be shown by cutting the pill open and exposing the mass to gentle heat in the dark. It should "phosphoresce"—*i. e.*, emit light. Sometimes it is given in a solution in almond oil of 1 per cent. strength. *Spiritus phosphori* is an official solution in absolute alcohol of about 0.1 per cent. strength. An *ethereal* solution is also used.

Toxicology.—As alkaline and earthy phosphates, it is a constituent of the tissues and fluids of the human body; it is found largely in the bones as calcium phosphate and in the nervous centers as a compound with fat and albumin. Ever since it was first used to tip lucifer matches its poisonous properties have been known; indeed, on the Continent of Europe it has been the favorite rat poison. While the other active poisons are guarded by law from general distribution, this one is easily obtained as the heads of matches and as "rat-paste," which contains from 1 to 4 per cent. of phosphorus mixed with oil, flour, sugar, and coloring-matter.[1] It is rarely used by homicides, but frequently by suicides, and

[1] *Coster's Rat and Roach Exterminator* contains 2.13 per cent. of phosphorus, and though the buyer is assured by the label that it is "not poisonous," 2 fatal cases have been reported from taking it. *Parson and Co.'s Vermin Exterminator* has 0.4 per cent. of free phosphorus.

sometimes children ignorantly eat the paste or suck the heads of matches. More than half the death cases are children. Of the adults, nearly all are suicidal, a few only being accidental and none criminal. In spite of the garlicky taste and smell, it could be given in coffee, the more easily if at the same meal onions or garlic had been eaten.

Symptoms.—If the phosphorus be taken in lumps, the effect is not proportionate to the weight. To be fully effectual it must be dissolved or finely divided, as it is in the rat-pastes and pill-masses.

The cases of poisoning are often referred by their symptoms to one of the three classes established by the researches of Tardieu—a common form, showing symptoms of local irritation and jaundice; a hemorrhagic form like scurvy, in which jaundice and effusions of blood occur; and a nervous form, in which jaundice is accompanied by creeping sensations, cramps, drowsiness, delirium, and convulsions.

Nearly 90 per cent. of the cases suffer from *acute irritation* followed by *jaundice* and *profound blood changes.* Complaint is made that the substance taken had the taste and odor of garlic. Sometimes violent pain in the throat, gullet, and stomach is experienced immediately, accompanied by vomiting and purging. The breath is phosphorescent, and the ejected matters may be bloody, garlicky in odor, and emit light when stirred in a shallow dish. In a large number of cases there is an interval of several hours between the taking of the poison and any symptom whatever.

Death from collapse may come at this early stage, but usually the irritation abates and *jaundice* sets in after a period of comparative comfort. This quiet interval usually lasts from two to three days, but it may be only one day in length or be prolonged for several weeks. The jaundice portends more or less profound *blood changes.* In addition to the general effects wrought by the biliary matters in the circulation there will be the toxic symptoms, caused by the presence of phosphorus derivatives. Given in detail, there will be yellowness of skin and conjunctiva and tenderness over the liver, with an increased area of hepatic dulness. Headache, insomnia, and itching eruptions of the skin are common. The urine is saffron-yellow or olive-green in color from the presence of bile-pigments, scanty, albuminous, bloody, containing tube-casts and occasionally leucin and tyrosin. Extreme weakness culminating in *heart failure* is a characteristic due to the degenerations of the muscular tissue, including the heart. These stormy signs soon culminate in delirium, convulsions, coma, syncope, and death.

In a certain proportion of cases, not necessarily fatal, the toxic effects on the blood and its vessels are made conspicuous by the *hemorrhages* which accompany the jaundice. Blood may be effused under the skin in spots or pass out by one or more of the mucous channels. Hemorrhage has occurred from the nose, mouth, bowels, kidneys, and bladder all at once. Women will have uterine hemorrhage, and if pregnant, will abort, with alarming flooding. Anemia and exhaustion reach an extreme stage, and delirium ending in death may supervene after months have elapsed since the administration of the poison. Even when the direct influence of the poison has passed away and life is no longer threatened, there may be persistent debility and local palsies.

The rarest form of acute poisoning is that in which the *nervous phenomena* are the most conspicuous. This form is likely to occur when the case is one of inhalation of fatal quantities of phosphorus vapor. In the preparation of "rat-paste," or in the making of matches, the materials may be accidentally heated so as suddenly to evolve large quantities of phosphorus vapor. The effects are fainting attacks, succeeded by profound prostration with extreme muscular weakness.

Emphasis must be laid upon the variety of symptoms, permitting of many different clinical pictures and also upon their insidious development. There can be but little doubt that at one time many cases were incorrectly diagnosed as acute yellow atrophy of the liver. This is not surprising, as the history of the case after the liver symptoms appear is the same as in acute yellow atrophy, even to the contraction of the organ itself. In a very small proportion of cases surviving a week jaundice does not occur. Casper reports a case that lived for twelve hours, the only marked symptoms being one act of vomiting and a garlicky odor of the breath, which was luminous in the dark.

Fatal Dose.—In the treatment of nervous diseases the usual dose is $\frac{1}{50}$ gr. (0.0013 gm.) thrice daily, but some persons can bear gradual increase to as much as $\frac{1}{4}$ gr. (0.016 gm.). It would be risky to begin with these maximum quantities, as the subjects of nervous diseases are usually very susceptible. A lunatic died from the effects of 0.0116 gm. (less than $\frac{1}{5}$ gr.).

A healthy adult would have his life put in jeopardy from 1 gr. taken in a finely divided form, such as the pill, paste, or the match-head. A child is reported to have died from sucking the heads of two matches, containing about $\frac{1}{50}$ gr. of phosphorus. On the other hand, there has been recovery after ten packages had been sucked.

Fatal Period.—Death has occurred in less than one hour, but the duration of life is very diverse in different cases. Some die

in four hours; three-fourths of the cases die within a week; some cases become chronic, the patient dying a lingering death after many months.

Treatment.—In considering the best remedial procedures it must be noted that great differences have been observed in the time of onset of the symptoms. In the majority they commence after an interval of from two to six hours; in a few they are described as immediate; in four-fifths they come on within six hours. In every case presenting a history of a poisonous dose the treatment should be instituted at once, instead of waiting for the symptoms to appear. There is need for instant evacuation by the stomach-tube, and washing out of the stomach with a solution of *potassium permanganate* of the strength of 0.5 to 1 per cent. (about 4 gr. to 1 fl. oz.), leaving about a pint in the stomach. This antidote has a chemical reaction with the phosphorus, by which the latter is said to be changed to harmless compounds. Potassium permangante oxidizes the phosphorus, forming phosphoric acid and phosphates, itself changing to manganese dioxid. In the absence of a stomach-tube the antidote should be given—4 gr. in 1 oz. of water—frequently repeated. The permanganate is in part reduced by the organic substances of the food, and hence the necessity of giving it in excess, although in a dilute solution to avoid gastric irritation. Better results have been obtained by washing out the stomach with warm water until the smell of phosphorus disappears, continuing with magnesia suspended in water or milk of magnesia. This is followed by copper sulphate or emulsion of turpentine, and later by sodium bicarbonate.

Copper sulphate is often recommended as an antidote. When its solution is mixed with phosphorus in a test-tube, the phosphorus is seen to change instantly to black copper phosphid, which is not injurious. There is one drawback to its use. In the quantities recommended and needed for full antidotal effect (3 gr. frequently repeated) the copper salt is a decided irritant, and is likely to aggravate the gastro-enteritis or set up a violent one of its own unless in very dilute solution.

Another antidote honored by text-book commendation is turpentine. It is said to combine with the phosphorus to produce phosphoroterebinthinic acid, a non-poisonous solid. To be efficient the article must be an old acid sample, and some enjoin that the French article alone is of any value. As old French turpentine is not the kind kept officially by druggists, it is practically out of the question.

After potassium permanganate or copper sulphate has been freely used for the phosphorus in the stomach, evacuation of the bowels should be secured by the use of some old turpentine that has been

kept for a long time on the shelf in doses of ½ fl. dr. (1.90 c.c.), given in an emulsion with mucilage every half hour. As the phosphorus tends to adhere to the mucous folds of the small intestine it is advisable to maintain purgation by giving the turpentine for several days.

Postmortem Appearances.—The general toxic effect of phosphorus is to induce a wide-spread degeneration of glandular and muscular tissue. This degeneration consists in the formation of fat in place of the true cellular tissue. It is presumable that those cases of death in which no change has been found postmortem would have yielded a different report if the microscope had been used to aid the naked eye. The *stomach* may be free from signs of disease, although, as a rule, there will be a fatty degeneration of the epithelial cells, with thickening of the mucous membrane, due to enlargement of the glands and an occlusion by large granular cells. This condition obtains in the intestines and is often associated with hemorrhagic foci and minute inflamed areas. These appearances are found also in diseases due to septic conditions of the blood.

Even at an early period the *liver* is the seat of fatty degeneration. If seen early, it may be enlarged, yellow, deficient in blood, and present a mottled section. Under the microscope the hepatic cells are found to lack definition and to be granular or filled with large fat-globules. When death follows a chronic history, the liver may be found atrophied and the changes more profound.

The capsule of the *kidney* is easily stripped. Under it are found hemorrhagic patches. The organ itself is enlarged, and its epithelial cells and vascular walls are infiltrated with granular fat.

The transverse stripes of the muscular fibers of the *heart* are replaced by fat, a form of change seen in the muscular system generally. If the case has been one of the hemorrhagic type, there will be extravasations of blood in the tubules of the kidney, in the endocardium, the peritoneum, the pleura, the mediastinum, and many other places.

Chronic Poisoning.—Weakly individuals working daily with white or yellow phosphorus itself, or even the less toxic but not inert *phosphorus sulphid*, P_4S_3, in match heads, become the subjects of "lucifer disease" or "phosphorus necrosis." After several weeks or months obstinate toothache is felt, and when the tooth is extracted the gum does not heal, but retracts, leaving a suppurating bony surface. Pieces of bone come away, and the disease-process in the marrow and in the periosteum spreads to new areas, other teeth and their sockets become involved, and greater portions of bone necrosed. Accompanying the local mischief, partly caused by it and also aggra-

vating it, is a general disturbance of health characterized by anemia pallor, weakness, hectic fever, diarrhea, septicemia, purpura, sometimes ending in death by exhaustion. These symptoms may be prevented by dental inspection of workmen and filling of all carious spots on the teeth, by the circulation of fresh air, by the frequent and systematic use of mouth-washes of sodium bicarbonate, and by the prompt exclusion of any one showing significant symptoms.

The exclusive use of "safety-matches" and non-toxic varieties is now ensured by legislation, and, with better hygienic measures, bids fair to remove "phossy jaw" from the bills of mortality.

Tests.—The tests for phosphorus are its peculiar odor, its luminous appearance in the dark, and the power of reduction possessed by it over silver nitrate.

Detection.—The garlicky odor is suspicious, but may be masked by articles of food having a similar odor, such as onions. If the room be darkened, the breath will shine faintly and phosphorescent spots will be seen upon the lips or clothing. The vomited matters or the urine, if put into a test-tube, acidulated with sulphuric acid, and gently heated, will evolve luminous fumes. A piece of white paper molded as a lid to the tube (Fig. 55) should be wet with a drop of a strong solution of silver nitrate. The phosphorus vapor will cause the metallic silver to be reduced as a black spot on the paper. To prove that this is not produced by hydrogen sulphid, the same test should be repeated after adding some lead acetate to fix the hydrogen sulphid in the liquid, or a plug of absorbent cotton wet with lead acetate may be put in the neck of the tube. When the phosphorus is present in minute quantities, it will not be evident by this test unless performed by the careful method of Mitscherlich.

Fig. 55.—Apparatus for testing phosphorus vapor with silver nitrate.

Mitscherlich's Test.—The suspected material is put into a flask (*c*, Fig. 56) and acidulated with sulphuric acid to prevent the escape of ammoniacal vapors. When heated gradually by the sand-bath the phosphorus vaporizes, and is conducted by a long delivery tube to a glass Liebig condenser, *d*, kept cold by water

circulating around the inner tube. The room being totally dark, flashes of light and shining clouds appear in the inner tube at the point where the phosphorus vapors are condensed by their cold surroundings. The odor of the distillate is alliaceous.

The tube being vertical, the condensed phosphorus will pass down into a receiver, *e*, where it may be converted to phosphoric acid by the action of nitric acid. The phosphoric acid precipitated by magnesian mixture, collected, ignited, and weighed, will determine the quantity of phosphorus.

If no luminosity has been observed after distilling one-third of the material, the remainder may be subjected to a more searching test. The end of the exit tube of the flask should be detached

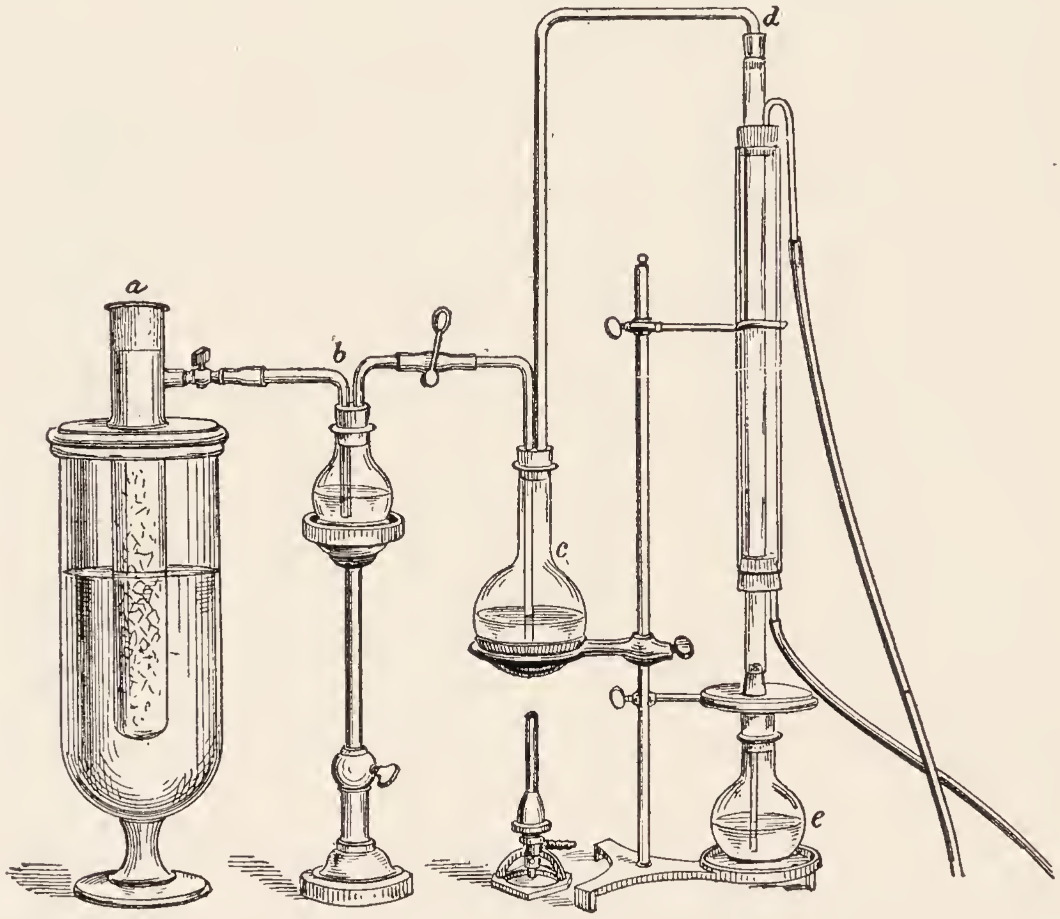


FIG. 56.—Mitscherlich's test for phosphorus: *a*, Generator for CO_2; *b*, wash-bottle; *c*, suspected material; *d*, condenser; *e*, receiver for distillate.

from the condenser at *d*, and immersed in a solution of silver nitrate. The contents of the flask, *c*, are again heated, while a continuous current of carbon dioxid from the generator, *a*, washed in *b*, passes through, slowly carrying the phosphorus unoxidized into the silver nitrate, precipitating black silver phosphid, and leaving some phosphoric acid in solution. Should no black deposit appear, the phosphorus may be assumed to be absent. The silver phosphid collected on a filter and washed is suspended in water, and introduced into the hydrogen apparatus employed in the phosphin test described below. The greenish flame is seen even when the quantity is very minute.

Fallacies.—Deductions based upon the detection of phosphoric

acid in the distillate when luminosity and free phosphorus have not been obtained may be erroneous. The phosphoric acid may have been brought over by mechanical action.

Interferences.—It can be performed in an organic mixture, but not in the presence of certain chemicals, such as iodin, calomel, and corrosive sublimate. The light will not show in the vapor of turpentine, which may have been given as an antidote. It is not perceived, should alcoholic or ethereal vapors arise from the same mixture. Ammonia, chlorin, hydrogen sulphid, sulphur dioxid, petroleum, creasote, and most essential oils interfere with the phosphorescence.

Delicacy.—This test is extremely sensitive, having yielded unmistakable evidence from $\frac{1}{50}$ gr. of phosphorus diffused in 3 oz. of fluid (1 : 200,000).

The Phosphin Test.—Having set up the usual hydrogen-generating apparatus—that is, flask, pure zinc, and dilute sulphuric acid—the gas is delivered by a three-way tube, having a side jet,

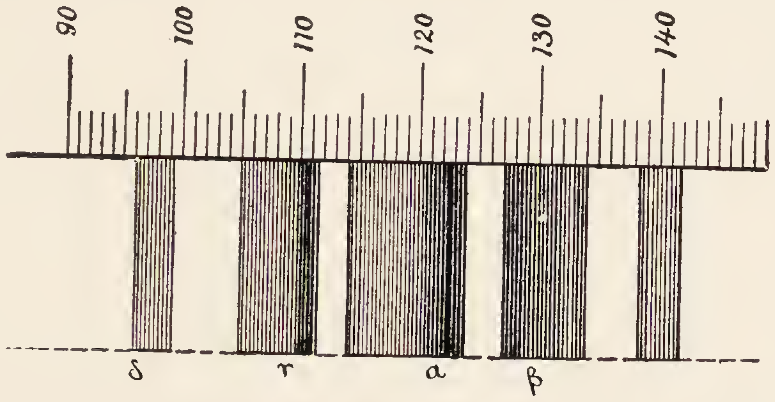


FIG. 57.—The bands represent the green lines of the spectrum of burning phosphin. They are between the lines *D* and *E* of the solar spectrum (Boisbaudran).

to a wash flask containing the suspected organic mixture, and gently heated. The nascent hydrogen acting on the phosphorus, phosphids, or its lower oxids in the mixture will form phosphin (PH_3), a gas which will escape from the heated flask by a tube drawn out to a jet and having a platinum tip. When lighted, the phosphin, if not too concentrated, will burn with a characteristic green color. It may be contrasted with the flame from the side jet, which should be the pale-blue hue of pure hydrogen. If this side jet is greenish, there must have been some phosphorus in the zinc of the generator. To make sure, the greenish flame should be studied with the spectroscope. If due to phosphorus, it will show one orange band between *C* and *D*, and several green bands (Fig. 57). Both the color of the flame and its spectrum are best developed if the temperature of the flame is not allowed to rise too high. This may be accomplished conveniently by allowing the flame to impinge against the bottom of a porcelain dish filled with cold water, or by wrapping the burner with a small strip of cloth saturated with cold water.

Phosphorescence in Hydrogen.—This test for free phosphorus only is best performed with the apparatus of Mukerji (Fig. 58), made from a three-necked Woulfe's bottle of 1-liter capacity, by inserting through close-fitting stoppers a long safety funnel tube (*a*) in one side-neck, and a short jet tube (*c*) in the other. Through a loose-fitting one at the middle neck rises a tube 11 in. long and ½ in. in diameter, which is closed above by a cork (*b*). From zinc and dilute sulphuric acid in the bottle hydrogen is evolved. Observed in the dark, the gas at the jet should emit no glow, even if commercial chemicals are used. When the chemical action has heated the bottle, the suspected material is introduced through the middle tube or through either neck, quickly closing again with the stopper.

Free phosphorus is vaporized and glows in a sheaf of light at the jet. If the middle cork is removed, the light sinks down through the jet into the bottle, and the glow appears at the outer opening of the middle tube.

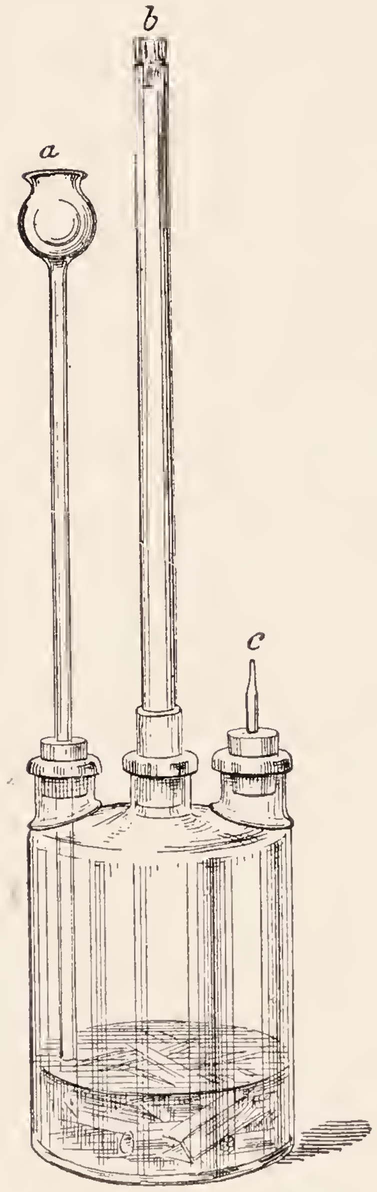


Fig. 58.—Phosphorescence in hydrogen.

Replacing the cork causes the glow to reappear at the jet. If a quantitative estimate is desired, a proper delivery tube may be substituted for the jet and the gas passed into silver nitrate.

Special Advantages.—The apparatus is simple, and as no lamp is required for distillation, complete darkness is possible. The amount of air entering by the jet tube is so small in comparison with the quantity of hydrogen continuously evolved that the mixture is never explosive. Before taking apart, the apparatus should be filled with water by the funnel tube.

While this test gives a glow with free phosphorus only, and not with any of its compounds, the *phosphin test* gives a green flame on ignition of the gas when the materials contain phosphorus, phosphids, phosphites, or hypophosphites indifferently. Free phosphorus does not unite with free hydrogen, and the gas here is not phosphin.

Interferences.—Turpentine or ether will prevent the glow in this test. It can be performed in the presence of organic matter, alcohol, iodin, hydrogen sulphid, and many other substances that prevent the glow in Mitscherlich's test.

Delicacy.—Mukerji found the test as sensitive as that of Mitscherlich, getting appreciable effects from 1 : 200,000.

Quantitative Estimation.—Sonnenschein's method for free phosphorus is first to estimate the phosphoric acid by diluting the suspected mixture, filtering a measured fraction, and precipitating with magnesian mixture, estimating as ammoniomagnesian phosphate. Another portion treated on a water-bath with potassium chlorate and hydrochloric acid will have its free phosphorus oxidized to phosphoric acid. This, being estimated, will show an excess over the first portion. The excess is then to be calculated as free phosphorus.

Period for Postmortem Recognition.—Tested by Mitscherlich's method, characteristic phosphorescence has been obtained in putrid organs two months after death and burial. There has been failure, however, to detect the poison even a few days after death, because of the conversion of the phosphorus into ammoniomagnesian phosphate or some other salt of no medicolegal interest.

Phosphorus and **hydrogen** form three compounds, to all of which the name phosphoretted hydrogen is applied, namely: PH_3, at ordinary temperatures a gas; PH_2, a liquid; and P_2H, a solid.

Phosphin (PH_3).—*Phosphorus terhydrid* or gaseous *phosphoretted hydrogen* when inhaled is a very poisonous gas, reducing the oxyhemoglobin of the blood. It can be made by boiling phosphorus with strong potash or soda lye, or by generating hydrogen in the presence of the lower oxids of phosphorus.

$$3KOH + 4P + 3H_2O = \underset{\text{Potassium hypophosphite.}}{3KH_2PO_2} + PH_3.$$

It is colorless, smells putrid, and, as ordinarily made, it contains another hydrid, PH_2, which causes it to inflame spontaneously on contact with the air. When evolved with hydrogen it burns with a greenish flame, but if dry and insufficiently supplied with air, the flame is white. When passed through a solution of silver nitrate, the silver is deposited as metal, leaving nitric and phosphoric acids in solution; by adding excess of molybdic acid the phosphoric acid can be detected.

Phosphorus and Oxygen.—When phosphorus burns in air it forms phosphorus pentoxid, P_2O_5. When the oxidation is incomplete three other compounds are made, thus: P_2O_4, the tetroxid; P_2O_3, the trioxid; P_4O, the suboxid.

Phosphorus pentoxid, or **phosphoric anhydrid,** is a white compound remarkable for its power of combining with water.

When its combining powers with water are fully satisfied, phosphoric acid results:

$$P_2O_5 \quad + \quad 3H_2O \quad = \quad \underset{\text{Phosphoric acid.}}{2H_3PO_4}$$

When the *trioxid* unites with water it forms phosphorous acid:

$$P_2O_3 \quad + \quad 3H_2O \quad = \quad \underset{\text{Phosphorous acid.}}{2H_3PO_3}$$

Phosphoric acid (H_3PO_4), or **orthophosphoric acid,** is the common acid used in medicine under the name *acidum phosphoricum.* The *dilute* official acid is made by mixing the strong with a sufficient quantity of water to make a 10 per cent. acid. The strong acid can be made by dissolving the pentoxid in water, or by the direct oxidation of phosphorus with strong nitric acid. The phosphates of the soils and of the animal and vegetable tissues are its salts.

Properties.—It is a non-corrosive, viscous liquid, colorless, odorless, with a pleasantly sour taste. It crystallizes with difficulty, when heated loses water, and at low redness volatilizes. It is a tribasic acid, forming three classes of salts, with a univalent metal. The point of transition as shown by litmus from acid to neutral reactions is not sharp when sodium hydroxid is added to dilute phosphoric acid. The alkaline indication appears before two hydrogen atoms are replaced. The alkalinity gradually increases until all the hydrogen has been replaced by the metal, and the normal salt produced is decidedly basic in reaction. The three salts possible with sodium are:

Na_3PO_4, normal, tertiary, or trisodium phosphate. It is an unstable and basic compound, alkaline in reaction.

Na_2HPO_4, secondary or disodium phosphate. Though retaining some acid hydrogen, yet this phosphate is feebly alkaline. It exists in the blood and is permanent.

NaH_2PO_4, acid, primary, or monosodium phosphate. It gives the acid reaction to urine.

The peculiar reactions to litmus shown by these salts are due to the difference in dissociation of the three hydrogen atoms. Perfect breaking down of H_3PO_4 into H^+, H^+, H^+, $(PO_4)^{\equiv}$ does not occur all at once in aqueous solution, nor readily at any time. While it does come eventually, the hydrogen ions, like those of other weak acids, are not completely dissociated in the beginning. The first ions of H_3PO_4 dissociate easily as H^+ and $(H_2PO_4)^-$. When the base sodium hydroxid is added to it the H^+ is removed, the second dissociation sets in, and the $(H_2PO_4)^-$ breaks down into H^+ and $(HPO_4)^=$. Further dilution or the action of more base separates

the anion $(HPO_4)^=$ into H^+ and $(PO_4)^{\equiv}$. This complete electrolytic dissociation is so slight that the water comes into play as it does with the other weak acids, and *hydrolytic dissociation* occurs, causing a different group of ions. In watery solution the interaction causes the normal sodium phosphate to break down in the manner indicated by the following equation:

$$Na_3PO_4 + H_2O = Na^+, Na^+, (HPO_4)^= + Na^+, (OH)^-.$$

The hydroxidion $(OH)^-$ thus liberated as a result of the two dissociations is the cause of the alkaline reaction of Na_3PO_4. The secondary phosphate, Na_2HPO_4, in water undergoes some degree of hydrolysis, and therefore gives a feebly alkaline reaction. With monad and dyad bases phosphoric acid forms double salts, such as ammoniomagnesian phosphate, NH_4MgPO_4, found in stale urine, and potassiobarium phosphate, $KBaPO_4$.

Tests for Phosphoric Acid and Phosphates.—(1) The phosphates are precipitated as white ammoniomagnesian phosphate by magnesia mixture (containing magnesium sulphate, ammonium chlorid, and ammonium hydroxid):

$$H_3PO_4 + MgSO_4 + 3NH_4OH = \underset{\text{Ammoniomagnesian phosphate.}}{MgNH_4PO_4} + \underset{\text{Ammonium sulphate.}}{(NH_4)_2SO_4} + 3H_2O.$$

(2) Ammonium silver nitrate throws down a yellow precipitate of silver phosphate which is soluble in ammonia and nitric acid:

$$H_3PO_4 + 3(AgNO_3, NH_3) = Ag_3PO_4 + 3NH_4NO_3.$$

(3) An excess of solution of ammonium molybdate in dilute nitric acid will precipitate the phosphoric acid if heated gently: the yellow precipitate is phosphomolybdate of ammonium.

$$(NH_4)_3PO_4,\ 10MoO_3,\ 2H_2O,$$

which dissolves easily in ammonia-water. This test, unlike (1) and (2), can be used in acid solution and is the most delicate.

Incompatibles of Acidum Phosphoricum.—It is incompatible with silver nitrate, ferric chlorid, lead acetate, and solutions of soluble iron phosphate or pyrophosphate. Dose 3 to 7 ♏ (0.20–0.66 gm.).

Metaphosphoric Acid (HPO_3).—*Properties.*—A transparent glassy mass, known as glacial phosphoric acid. It is a monobasic acid.

Preparation.—Metaphosphoric acid is formed when ortho-

phosphoric acid is heated higher than is necessary to produce pyrophosphoric.

Upon the addition of water to this glacial acid, a solution is obtained, which, upon boiling, is converted into the tribasic phosphoric acid, H_3PO_4.

It is detected by the precipitation of its barium salt as a white solid. A mixture of albumin with acetic acid gives a white precipitate to its solution.

Pyrophosphoric Acid ($H_4P_2O_7$).—*Properties.*—It can be obtained as crystals by evaporation *in vacuo*. It is tetrabasic.

Preparation.—Pyrophosphoric acid is prepared (1) by heating the tribasic phosphoric acid, H_3PO_4, to 213° C. (415.4° F.). Thus:

$$\underset{}{2H_3PO_4} = \underset{\text{Water.}}{H_2O} + \underset{\text{Pyrophosphoric acid.}}{H_4P_2O_7}$$

(2) By the action of hydrogen sulphid, H_2S, on pyrophosphate of silver, $Ag_4P_2O_7$. Thus:

$$Ag_4P_2O_7 + 2H_2S = \underset{\text{Sulphid of silver.}}{2Ag_2S} + \underset{\text{Pyrophosphoric acid.}}{H_4P_2O_7}$$

It is identified by the *white* precipitate falling upon the addition of silver nitrate, but no precipitate is caused by albumin and acetic acid.

The three acids above described may be prepared by acting upon phosphorus pentoxid, P_2O_5, with different proportions of water, as follows:

$P_2O_5 + H_2O = 2HPO_3$, Metaphosphoric acid, monobasic.
$P_2O_5 + 2H_2O = H_4P_2O_7$, Pyrophosphoric acid, tetrabasic.
$P_2O_5 + 3H_2O = 2H_3PO_4$, Orthophosphoric acid, tribasic.

By heating to 300° C. (572° F.) the tribasic phosphoric acid, $2H_3PO_4$, and thus driving off a molecule of water, we can obtain the pyrophosphoric acid, $H_4P_2O_7$, and by the action of heat to 400° C. (752° F.) upon this, with the loss of another molecule of water, we obtain the metaphosphoric acid, $2HPO_3$.

Phosphorous Acid (H_3PO_3).—*Properties.*—It forms deliquescent crystals which readily decompose; throws down gold, silver, and platinum from their solutions. As a colorless acid liquid it is dibasic, only 2 H atoms will ionize, as in the formula H^+, H^+, $(HPO_3)^=$. It is a strong deoxidizer, uniting with oxygen to form phosphoric acid. Its salts are called phosphites.

Preparation.—Phosphorous acid is formed by acting upon the trichlorid of phosphorus, PCl_3, with water, H_2O. Thus:

$$PCl_3 + 3H_2O = 3HCl + H_3PO_3.$$

Hypophosphorous Acid (H_3PO_2).—*Properties.*—An acid, syrupy fluid, is official, containing 30 per cent. of absolute acid. All the hypophosphites are soluble in water. It is a white crystalline substance, having but one atom of replaceable hydrogen. This may be expressed by writing it as H^+, $(PO_2H_2)^-$. The other hydrogen atoms have no acid quality and will not ionize.

Preparation.—This acid is prepared by acting upon barium hypophosphite, $Ba(H_2PO_2)_2$, with sulphuric acid, H_2SO_4. Thus:

$$Ba(H_2PO_2)_2 + H_2SO_4 = BaSO_4 + 2H_3PO_2.$$

Acidum hypophosphorosum dilutum contains 10 per cent. H_3PO_2. Dose 10 to 60 ♏ (0.66–4.00 gm.).

Phosphorus with chlorin forms two compounds, viz.: PCl_3, phosphorus trichlorid; PCl_5, phosphorus pentachlorid.

Phosphorus trichlorid, PCl_3, is a colorless, volatile, strongly fuming liquid, and is formed by passing chlorin gas over phosphorus. It gradually decomposes into hydrochloric acid and phosphorous acid. It may also be formed by the combustion of phosphorus in chlorin gas.

Phosphorus pentachlorid, PCl_5, is a solid crystalline substance, and decomposes by excess of water into hydrochloric acid, HCl, and tribasic phosphoric acid, H_3PO_4. It is prepared by passing excess of chlorin through the phosphorus trichlorid. Should water be present only in limited quantity, a liquid called *phosphoric oxychlorid*, PCl_3O, is formed. Thus:

$$PCl_5 + H_2O = 2HCl + PCl_3O.$$

Phosphorus forms with *iodin* PI_3 and PI_5, with *bromin* PBr_3 and PBr_5, and it burns spontaneously in those substances when they are in the gaseous state. By the action of sulphuretted hydrogen, H_2S, upon phosphorus pentachlorid, PCl_5, a substance termed *phosphoric sulphochlorid*, $PSCl_3$, is obtained.

Phosphorus forms several compounds with *sulphur*, two of them, P_2S_3 and P_2S_5, corresponding in composition with the oxids P_2O_3 and P_2O_5.

CARBONIC ACID

Formula, H_2CO_3. Molecular weight, 62.

In another section the element carbon and its two oxygen compounds, carbon monoxid and carbon dioxid, have been fully discussed. Mention was made of the fact that when dissolved in water carbon dioxid became carbonic acid, and in this form was widely known in the aërated liquid commonly called *soda water*. If the freshly drawn aërated water be tested before much gas

escapes, it will be found to give the usual red reaction with litmus. The gas CO_2, like SO_2, is an anhydrid, converted to an acid by water; H_2CO_3, resembling in this respect H_2SO_3, sulphurous acid. Like that acid, H_2CO_3 readily decomposes into H_2O and the anhydrid CO_2. Carbonic acid is a weak dibasic acid. It resembles H_2SO_3 and other dibasic acids—in that it breaks up into two different anions, first into the univalent $(HCO_3)^-$, and next into the divalent carbanion $(CO_3)^=$. Being a very weak acid, dissociation is very slight indeed, whether it be at the first stage, $H_3CO_3 = H^+, (HCO_3)^-$, or at the less appreciable second $(HCO_3)^- = H^+, (CO_3)^=$. The dominant anion appears to be $(HCO_3)^-$, the solution tending to form this group by preference.

The carbonates are very abundant in nature, among them being limestone, marble, and chalk; and they are in general quite insoluble in water. All carbonates, except those of the alkali metals, are of difficult solubility. Both the normal sodium carbonate, Na_2CO_3, and the acid salt, $NaHCO_3$ have an alkaline reaction. As this indicates the presence of hydroxidion $(HO)^-$ it appears that the soluble carbonates are hydrolyzed—that is, the ions are changed by interacting with the water. A part, at least, of this hydrolysis may be represented by the following equation:

$$Na_2CO_3 + H_2O = Na^+, (HO)^- + Na^+, (HCO_3)^-.$$

Obeying its tendency, the carbanion $(CO_3)^=$ breaks up the H_2O to form the ions $(HCO_3)^-$ and $(HO)^-$. A small amount of hydroxidion is sufficient to give an alkaline reaction to solutions of $NaHCO_3$. The reactions indicated above characterize all soluble carbonates.

DERIVATIVES OF CARBONIC ACID

Beside the numerous class of carbonates in which the hydrogen only is replaced by metals, there are important compounds which may be regarded as derived from carbonic acid by replacement of its hydroxyls in $CO(OH)_2$, with chlorin and with amidogen, NH_2. The two most important are carbonyl chlorid, $COCl_2$, and carbonyl diamid or urea, $CO(NH_2)_2$.

Carbonyl Chlorid ($COCl_2$) (*Carbon Oxychlorid*).—This compound is known as *phosgene gas* because it is generated by the action of direct sunlight on a mixture of equal proportions of carbon monoxid, CO(carbonyl), and chlorin, $CO + Cl_2 = COCl_2$. The same reaction occurs by catalysis when the mixed gases are passed over charcoal (p. 386).

Properties.—Carbonyl chlorid is a gas without color, but with a stifling odor. When inhaled it is a suffocative poison (p. 389).

In the presence of water it is decomposed with the formation of carbonic acid and hydrochloric acid:

$$COCl_2 + 2H_2O = H_2CO_3 + 2HCl.$$

Carbonic Acid Diamid.—The most significant reaction of carbonyl chlorid is one by which we may infer the constitution of urea. When ammonia is permitted to act on $COCl_2$ there is decomposition of the carbonyl chlorid with formation of ammonium chlorid and a compound containing carbonyl and two parts of the group NH_2, characteristic of amids, thus:

$$COCl_2 + \underset{\text{Ammonia.}}{4NH_3} = \underset{\text{Carbonyl diamid.}}{CO(NH_2)_2} + \underset{\text{Ammonium chlorid.}}{2NH_4Cl}$$

By extracting with alcohol the carbonic acid diamid is separated from the insoluble ammonium chlorid, and on evaporation is left as colorless crystals. These crystals are neutral in reaction, without odor, but having a bitter taste. In solution they have no electroconductivity, hence are non-electrolytes.

This substance is found abundantly in the body and urine of carnivora, and is known commonly as *urea*.

Carbon Disulphid (CS_2).—The relationship of carbon dioxid, CO_2, to carbonic acid, $CO{<}^{OH}_{OH}$, has already been referred to. There is a trithiocarbonic acid, $CS{<}^{SH}_{SH}$, in which all the oxygen has been replaced by sulphur, and it has a corresponding disulphid, CS_2. This is prepared by passing vapor of sulphur over heated charcoal. It is a highly refractive, colorless, volatile, inflammable liquid, neutral in reaction, with a peculiar odor. It boils at 46° C. (115° F.). It is not miscible with water, but freely dissolves in alcohol, ether, and chloroform. It is a valuable solvent for iodin, phosphorus, sulphur, etc.

Toxicology.—Owing to its employment in the manufacture of vulcanized rubber, cases of chronic poisoning from inhaling the vapor are not rare. Workmen exposed to it in imperfectly ventilated factories experience at first a form of excited intoxication characterized by vivacious talking, singing, immoderate laughter, causeless weeping, and delirium. They also complain of headache, vertigo, and muscular cramps. If the person does not change his occupation the second stage appears, in which there is headache, drowsiness, melancholy, weakness, and loss of feeling in the extremities, ending in paralysis.

THE CYANOGEN GROUP

One of the simplest compounds of carbon is the gas cyanogen, C_2N_2, formed when carbon and nitrogen unite in the heat of the electric arc. All of its derivatives contain the group CN, just as the chlorids, hypochlorites, etc., contain Cl.

Many of its compounds have properties resembling those of the chlorin family, though they contain this univalent *group of atoms*, CN, in place of the *single atom*, Cl. Sometimes it is written Cy, to indicate that the group CN acts like a single element, just as NH_4 behaves like the single atom of an alkaline metal.

The term *compound radical* is applied to a group playing the part of an atom. The relation between HCN and HCl is shown by the following examples, in which H or a metal is the electro-positive *simple radical* and CN the electro-negative *compound radical.*

$$HCl,\ KCl,\ AgCl,\ HgCl_2,\ HOCl.$$

$$HCN,\ KCN,\ AgCN,\ HgC_2N_2,\ HOCN.$$

Preparation.—Cyanogen is prepared by heating mercuric cyanid to a red heat in a hard glass reduction tube, connected by a perforated cork and delivery tube with a trough of mercury:

$$HgC_2N_2 = Hg + C_2N_2.$$

Mercury is deposited upon the cool portions of the tube.

Properties.—The free gas is colorless, condensing to a liquid under a pressure of four atmospheres; it has a characteristic odor, is an active poison, and burns with a purple flame into carbon dioxid and nitrogen. It is soluble in water and alcohol, but its aqueous solution is unstable, depositing a brownish precipitate.

Hydrocyanic Acid (HCN) (*Prussic Acid*).—This compound is sometimes called *absolute*, *pure*, or *anhydrous*, to distinguish it from the official form, *acidum hydrocyanicum dilutum*, which contains not less than 2 per cent. of the anhydrous, according to the pharmacopeias of U. S., Great Britain, Prussia, Switzerland, and Norway. The French official article contains 10 per cent., which is the average strength of Scheele's acid. They are all so unstable that in any but fresh specimens the strength is uncertain. The following parts of plants can be made to yield HCN by appropriate treatment: wild-cherry bark; flowers and leaves of the laurel and the peach; kernels of peach, plum, apple, cherry, and apricot; the bark, leaves, flowers, and fruit of the wild service tree (*Prunus padus*); the leaves and flowers of the shrubby spiræa. These and other plants contain amygdalin, a glucosid found abundantly in

Amygdala amara, the bitter almond. When the vegetable tissue is bruised or chewed, amygdalin is brought into contact with emulsin, an enzyme which in the presence of water breaks up the amygdalin into hydrocyanic acid and other compounds:

$$\underset{\text{Amygdalin.}}{C_{22}H_{27}NO_{11}} + 2H_2O = \underset{\text{Hydrocyanic acid.}}{HCN} + \underset{\text{Glucose.}}{2C_6H_{12}O_6} + \underset{\text{Oil of bitter almonds.}}{C_7H_6O}$$

According to Liebig and Wohler, 17 gm. of amygdalin yield 1 of hydrocyanic acid and 8 of oil of bitter almonds.

Oleum amygdalæ amaræ contains 2 to 4 per cent. of hydrocyanic acid.

Preparation.—Prussic acid can be prepared by the action of hydrochloric acid on silver cyanid:

$$\underset{\text{Silver cyanid.}}{AgCN} + HCl = AgCl + \underset{\text{Hydrocyanic acid.}}{HCN}$$

The silver chlorid is precipitated, and the acid collected in the filtrate. Usually it is made by distilling potassium ferrocyanid or cyanid with sulphuric acid, just as hydrochloric acid is made by the action of sulphuric acid on sodium chlorid.

$$\underset{\text{Potassium cyanid.}}{KCN} + H_2SO_4 = HCN + KHSO_4.$$

The dilute acid (2 per cent.) is the only form used in medicine. Its dose is 1 to 5 ♏ (0.12–0.33 gm.), repeated at short intervals. It is incompatible with salts of copper, iron, and silver. When it turns brown it is unfit for use.

Properties.—Absolute or anhydrous prussic acid is a colorless volatile liquid with an odor like oil of bitter almonds. It reddens litmus feebly, dissolves freely in water, but the solution rapidly separates a brown substance and changes to ammonium formate:

$$HNC + 2H_2O = \underset{\text{Ammonium formate.}}{NH_4H.CO_2}$$

It is a poison so powerful and unstable that it is not kept in the drug-stores in its anhydrous form.

Toxicology.—The least quantity that has destroyed life is $\frac{1}{2}$ fl. dr. of the official dilute acid or $\frac{6}{10}$ gr. of the anhydrous acid. The inhalation of the vapor has produced death. Recovery has occurred after taking 1 fl. dr. of Scheele's acid, and in another case after 2 fl. dr. of the official acid, which, if not deteriorated, should have been equal to 2.4 gr. of anhydrous acid.

Symptoms.—Prussic acid is a retarding catalyzer—*i. e.*, by its presence prevents oxidation and other vital processes important to the life of the organism. It depresses the nutrition of protoplasms in plants and animals. Applied externally, care must be exercised lest the poison enter by open cuts. The anhydrous acid has been used as a local application for allaying oversensitive conditions of the cutaneous nerves. Instant death may follow large doses by the mouth or the inhalation of vapor of the strong acid.

If death is not instantaneous, then in a few seconds there will be giddiness, relaxed muscles, causing a fall to the earth, convulsions, stertorous breathing, slowing of the pulse, closed jaws, clammy skin, odor of bruised peach-kernels on the breath, dilated pupils, asphyxia, stupor, ending in coma. In some cases the resemblance to apoplexy is so marked as to cause mistake in diagnosis. Insensibility is not always immediate, though death is usually preceded by convulsions and coma. Death is due to arrested respiration.

Fatal Period.—In most cases ten minutes elapse before death. Consciousness may be lost in a few seconds, the suicide falling dead in two minutes.

It is possible that life may be prolonged for three hours and a half, but in most cases if the patient live an hour he will recover.

Treatment.—If strong prussic acid has been taken there is rarely time for treatment. After potassium cyanid or the dilute acid there may be opportunity for the following procedure:

Give prompt emetics, such as mustard and water, aided by tickling the throat.

By the flexible tube, siphon out the stomach with Kobert's antidote—dilute solution of hydrogen peroxid, which slowly converts HCN into relatively harmless oxamid:

$$2HCN + \underset{\text{Hydrogen peroxid.}}{H_2O_2} = \underset{\text{Oxamid.}}{C_2O_2N_2H_4}$$

If potassium cyanid was the form of poison, add vinegar to the hydrogen peroxid. Should death be delayed there may be time for the antidote of potassium carbonate, gr. xx, dissolved in water, f℥j, followed with a mixture of ferrous sulphate, gr. x, and magnesia, gr. xxx, in water, f℥j. The poisonous anion cyanidion, $(CN)^-$, is changed to ferrocyanidion, $Fe(CN)_6^{\equiv}$, which is not poisonous in the presence of an alkali.

In mining and photographic laboratories the materials for this antidote should be kept made up in packages and the stomach tube be always at hand for use without delay.

Cold affusions over the face and chest and inhalations of

ammonia may be assisted by brandy subcutaneously administered, frictions to the extremities, and artificial respiration.

Atropin, $\frac{1}{60}$ gr., may be given hypodermically as a stimulant to heart and respiration.

Postmortem Appearances.—The odor of bruised peach-kernels may be noticed in the room or on the body. There are no characteristic lesions, but most frequently there is engorgement of the venous system, the arteries being empty. The postmortem stains are bright pink, due to the cyanohematin of the blood and to the fact that the tissues cannot take up the oxygen of the blood, leaving it red even in the veins.

Tests.—*Silver nitrate* produces a white precipitate, soluble in boiling, strong, nitric acid:

$$HCN + AgNO_3 = HNO_3 + AgCN.$$

This white silver cyanid is distinguished from the chlorid by being only sparingly soluble in ammonia, by its not turning dark on exposure to light, and by giving off cyanogen gas when heated, the cyanogen burning with a purple flame. Under a lens the cyanid may appear as prismatic needles, while the chlorid is amorphous.

The most delicate test is this one used on HCN in the state of vapor. The suspected matters are put in a beaker which is immersed in a basin of warm water. The mouth of the jar is covered with a watch crystal, which has on its concave under side a drop of weak solution of silver nitrate. Hydrocyanic-acid vapor causes a white film over the drop, which, if slowly formed, will be seen by the microscope to consist of delicate crystalline prisms. If putrefaction has set in, the test cannot be used, as the black silver sulphid masks the white cyanid.

Prussian-blue Test.—On the addition of potassium hydroxid, followed by fresh ferrous sulphate and ferric sulphate, a greenish-blue precipitate forms, which is turned to a clear Prussian blue by the addition of hydrochloric acid.

$$18HCN + 18KOH + \underbrace{5FeSO_4}_{\text{Ferrous sulphate.}} + \underbrace{Fe_2(SO_4)_3}_{\text{Ferric sulphate.}} + H_2SO_4 =$$
$$9K_2SO_4 + \underbrace{Fe_4(Fe(CN)_6)_3}_{\text{Ferric ferrocyanid.}} + 18H_2O + H_2.$$

Ammonium-sulphid test may be used upon fluids in a test-tube, but gives best results with the vapor of HCN, even after putrefaction has begun. The stomach contents or other suspected matter are put in a jar which is immersed in warm water, and the mouth closed with a glass plate carrying a drop of ammonium

hydrosulphid. A white ammonium thiocyanate soon appears in this drop on the under side. This drop is then evaporated almost to dryness and touched with a drop of ferric chlorid, when it develops a blood-red color, which is discharged after treating with mercuric chlorid:

$$\underset{}{HCN} + \underset{\text{Ammonium hydrosulphid.}}{NH_4HS} = 2H + \underset{\text{Ammonium thiocyanate.}}{NH_4SCN}$$

$$3NH_4SCN + \underset{\text{Ferric chlorid.}}{FeCl_3} = \underset{\text{Ammonium chlorid.}}{3NH_4Cl} + \underset{\text{Iron sulphocyanate.}}{Fe(SCN)_3}$$

Detection.—If death has been recent, the odor of peach-kernels may be perceived. The stomach, its contents, and other tissues should be distilled at a low temperature without acidulating, as acids may form a cyanid by decomposing the normal potassium thiocyanate of the saliva.

Instead of acidulating the suspected matter before distillation, *Jacquemin's process* is to mix it with a concentrated solution of sodium bicarbonate, which evolves CO_2, a gas that promotes the escape of HCN and liberates HCN if potassium cyanid be present, but does not decompose potassium thiocyanate nor potassium ferrocyanid nor other non-poisonous cyanids.

Any of the above tests may be applied to the vapor, or the distillate in the receiver may be treated with potassium hydrate and tested for potassium cyanid by silver nitrate. The resulting silver cyanid is washed, dried, and weighed. For every 100 parts of AgCN we may calculate 20.15 parts of anhydrous HCN.

Potassium Cyanid (KCN).—This compound figures quite frequently as a poison, because of its extensive use in the arts of photography and electroplating, and in the extraction of gold from its ores by the cyanid process.

Properties.—It occurs in opaque, white, strongly alkaline, deliquescent masses, which have the taste of bitter almonds, and in contact with the air are decomposed by CO_2 with the slow formation of hydrocyanic acid, recognized by the odor.

As hydrocyanic acid is a weak acid, its salt is hydrolyzed by the water, forming hydroxidion, which is alkaline, and hydrogen cyanid, which is scarcely dissociable, and hence is given off as molecules with the characteristic odor. This is in accordance with the equation:

$$KCN + H_2O = K^+, (OH)^- + HCN.$$

It is soluble in two parts of water, and is sometimes used in medicine as a sedative in doses of $\frac{1}{20}$ to $\frac{1}{8}$ gr. Its *incompatibles* are

acids; iodin; salts of lead, mercury, and silver; chlorates; nitrates; permanganates; alkaloids; chloral hydrate.

Toxicology.—*Symptoms.*—Its physiologic effects are like those of hydrocyanic acid. The convulsive and narcotic symptoms are often preceded by those of gastric irritation, such as pain and vomiting. The onset of symptoms is slower than by the acid, thus giving more time for treatment.

The *treatment* is practically the same as that given for the acid, p. 196.

Postmortem Appearances.—There is usually marked congestion of the stomach, due to the strongly alkaline salt. A bright red hue is observable in the throat, esophagus, and stomach, due to the formation of cyanohematin by the penetration of the salt to the blood in the tissues.

Tests.—When treated with dilute acids potassium cyanid is quickly decomposed, and to the vapor the various tests for hydrocyanic acid may be applied. *Silver nitrate* reacts directly, precipitating white silver cyanid; and the potassium is detected by platinum chlorids. In making the *Prussian-blue test* the potassium hydrate must be omitted, unless followed by excess of HCl.

Other Cyanids.—The soluble metallic cyanids and methyl cyanid are all poisonous, as they dissociate the active anion $(CN)^-$. If the cation be poisonous also, as in mercury cyanid, $Hg^+, (CN)_2^-$, the symptoms will be those of an irritant mercurial salt in addition to those of potassium cyanid.

Poisonous, also, are the chlorid and iodid of cyanogen. In neutral or alkaline menstrua the double cyanids, not having as anion, cyanidion, (CN), but ferrocyanidion, $Fe(CN)_6^{\equiv}$, are considered relatively harmless. It must not be forgotten that in the presence of acids the iron of $Fe(CN)_6^{\equiv}$ may be taken up, and the (CN) group be freed to do its deadly work.

In cyanic acid and its salts, the cyanates, the anion is not $(CN)^-$, but $(OCN)^-$, which is not poisonous. The thiocyanates are not seriously injurious, as they have the anion $(SCN)^-$.

Cyanic acid, H . OCN, is a strongly acid, unstable liquid, forming cyanates. In water it quickly changes to acid ammonium carbonate:

$$HOCN + 2H_2O = (NH_4)HCO_3.$$

Potassium cyanate, KOCN, is formed when potassium cyanid slowly oxidizes in the air, though it is usually prepared by heating KCN with a reducible metallic oxid and then extracting the product with dilute alcohol:

$$KCN + PbO = KOCN + Pb.$$

It is a colorless crystal and readily soluble. When its solution is mixed with ammonium sulphate, *ammonium cyanate* is formed:

$$2KCNO + (NH_4)_2SO_4 = \underset{\text{Ammonium cyanate.}}{2(NH_4) . CNO} + K_2SO_4.$$

If the resulting solution be evaporated on a water-bath, the ammonium cyanate is transformed into *urea*. It was in this way that Wöhler first produced urea by artificial synthesis. There is no addition or subtraction of atoms, as the two substances have the same molecular formula. The change is termed *intramolecular* and may be expressed by the constitutional formulas given below:

$$\underset{\text{Ammonium cyanate.}}{NH_4 . O . CN} = \underset{\text{Urea or carbonyl diamid.}}{CO(NH_2)_2}$$

It is believed that there is a migration of atoms to differently arranged groups. The two bodies are said to be *isomeric—i. e.*, although they have the same composition their properties differ because of a difference in arrangement of the atoms.

OXALIC ACID (Acid of Sugar)

Formula, $C_2H_2O_4 + 2H_2O$. Molecular weight, 125.7.

Oxalic acid and its salts are widely present in nature, being found in various plants, such as rhubarb (used for pies), nightshade, dock, sorrel (*oxalis*) (used for greens), and in animals also, occurring not infrequently as a constituent of the human urine. In the latter it is incidental to the gouty condition and some forms of dyspepsia, occurring as calcium oxalate in the form of a whitish deposit made up of microscopic crystals, octahedral or dumb-bell shaped, and insoluble in warm water and in acetic acid (p. 607).

Preparation.—As a sodium salt it may be prepared by passing carbon dioxid over sodium heated carefully:

$$\underset{\text{Sodium.}}{Na_2} + \underset{\text{Carbon dioxid.}}{2CO_2} = \underset{\text{Sodium oxalate.}}{Na_2C_2O_4}$$

It can be prepared from sugar by oxidation with nitric acid, and, therefore, is sometimes known in the arts as *acid of sugar*.

$$\underset{\text{Sugar.}}{C_{12}H_{22}O_{11}} + 9O_2 = \underset{\text{Oxalic acid.}}{6C_2H_2O_4} + 5H_2O.$$

Its bleaching properties and solvent powers for metallic oxids make it useful to dyers and workers in leather, makers of straw hats and bonnets, and workers in marble and in brass. About the home it is used to remove ink-stains from linen. Druggists dispense it at a low price, and consequently the would-be suicide

not infrequently resorts to it. Its resemblance to Epsom salts leads to accidental poisoning, but the very sour taste is likely to betray the homicide, who rarely resorts to it except when it can be masked by some other sour beverage.

Properties.—The crystals of oxalic acid are colorless, four-sided, prismatic, not deliquescent, and so closely resemble in appearance those of magnesium sulphate and zinc sulphate that it is often confounded with them. These crystals are very acid, soluble in about 10 parts of cold water and in 2½ of cold alcohol, but very sparingly in ether. Heated on porcelain or platinum, they sublime without residue. They contain two parts water of crystallization.

It can be distinguished from the substances for which it is sometimes mistaken by the following ready tests, applicable in the household:

	Oxalic acid.	Magnesium sulphate.	Zinc sulphate.
Taste	Sour.	Bitter, nauseous.	Bitter, metallic.
Reaction	Very acid.	Neutral.	Slightly acid.
Heated	Sublimes.	Fixed.	Fixed.
Sodium carbonate	No precipitate, but effervescence.	No effervescence, but a white precipitate.	No effervescence, but a white precipitate.
Iron, ink	Bleaches.	No effect.	No effect.

As it is a dibasic acid it makes two salts with univalent metals. With potassium it forms KHC_2O_4 and $K_2C_2O_4$.

Potassium Binoxalate (KHC_2O_4,H_2O) (*Acid Oxalate*).—This salt is usually dispensed by druggists to remove rust and ink-stains from linen, to bleach straw, and to polish metals, under the very deceptive name of "essential salts of lemon" and "salts of sorrel," and sometimes without even the "grim heraldry of death" usually blazoned on labels for poisonous substances. It is sometimes dispensed as a white powder, although it crystallizes in colorless rhombic prisms, having 1 part of water of crystallization. It has a decidedly acid reaction and sour taste, and is soluble in 40 parts of water. It is likely to be mistaken for cream of tartar, which is also a sour white solid. Almost equal to oxalic acid in the violence of its poisonous action, its symptoms, postmortem appearance, antidotes, and detection are practically the same.

The same may be said in lower degree to be true of the *neutral potassium oxalate* ($K_2C_2O_4$), which is white, crystalline, soluble in water and neutral in reaction. Not being used in the household it does not figure in toxicology, though when absorbed it is a violent neurotic poison.

Toxicology.—*Symptoms.*—Like the acid, soluble oxalates combine with the calcium of the tissues and derange their equilibrium. The symptoms vary considerably in different cases, but can be conveniently classified as, first, those due to the *local* erosive action on

the mucous surfaces, and, second, those arising from the *remote* impression upon the nervous system—convulsive and narcotic. The symptoms produced by the local action of a large amount of a strong solution are very sour taste, thirst, pain, and burning in mouth, throat, and stomach, difficult swallowing, vomiting of black or bloody substances, collapse. Occasionally pain is absent. Sometimes death may occur without vomiting.

"If," says Christison, "a person immediately after swallowing a solution of a crystalline salt which tasted purely and strongly acid is attacked with burning in the throat, then with burning in the stomach, vomiting, particularly of bloody matter, imperceptible pulse and excessive languor, and dies in half an hour, or still more in twenty, fifteen, or ten minutes, I do not know any fallacy which can interfere with the conclusion that oxalic acid was the cause of death. No parallel disease begins so abruptly and terminates so soon, and no other crystalline poison has the same effect."

A case of oxalic-acid poisoning occurred in a boy aged fifteen years. Twelve minutes after the poison had been swallowed the patient was unconscious, the skin pallid and clammy, and his extremities cold. The radial pulse could not be felt. The pupils were fairly dilated. The jaw was fixed in tetanic spasm, and froth exuded from between the teeth. One-tenth of a grain of apomorphin was injected hypodermically; a stomach siphon-tube was introduced after the jaws had been forced apart, and 1 pint of warm water was placed in the stomach, but immediately expelled. Vomiting continued, and consciousness returned. The boy was given ½ oz. of powdered chalk, suspended in water, and this also was shortly ejected. Recovery proceeded under stimulation. The quantity of poison taken was upward of 2½ drams.

If, owing to the smallness of the dose, death is not prompt, absorption of the poison ensues, and then the remote or *neurotic* symptoms appear. These are headache, cramps, convulsions, delirium, and coma. If the patient survive, there may be numbness and tingling, with loss of voice, lasting for weeks. When a small dose has been taken in dilute solution, the symptoms have not come on for hours, and then the nervous phenomena are more prominent.

Fatal Dose.—The least weight of the acid recorded as having fatal consequences is 1 dram (3.88 grams). Statistics show that the dose most likely to prove fatal is from ½ to 1 oz. Early vomiting and a measure of relief are caused by excessive doses. More than 1 oz. (14.2 gm.), if retained, usually causes death, although recovery has occurred after a dose of 2 oz.

If efficient antidotes are instantly given there may be recovery from much larger doses, although the majority of cases prove fatal.

Fatal Period.—In 1 case death, supposed to be due to gastric hemorrhage, occurred without pain in *three minutes.* In other cases surviving the acute action on the alimentary tract death has occurred from coma after several days, 1 living until the twenty-third day.

Treatment.—The chemical antidotes are finely divided chalk or calcined magnesia or its carbonate, suspended in a large quantity of water, and followed by free drafts of warm water to facilitate vomiting. As the toxic action is prompt, the antidote must be given at once. With a shovel or a kitchen knife the wall-plaster can be scraped off and used as an impure calcium carbonate.

Oxalic acid is chemically neutralized by the alkalies as well as by the alkaline earths (lime and magnesia), but the alkaline oxalates, being soluble and poisonous, are inadmissible, while the oxalates of calcium and magnesium are insoluble and innocuous. Emetics may be necessary (such as 5 drops of a 2 per cent. solution of apomorphin hydrochlorate). If the stomach-pump have a hard tube it is likely to injure the eroded lining of the gullet and stomach.

Postmortem Appearances.—Colored stains upon the lips and face are absent, but the lips, tongue, throat, and gullet are usually white, and the lining membrane is loose, eroded in patches, and contracted into folds. Sometimes the stomach is black from extensive venous engorgement and contains blood or a brownish, grumous material; sometimes the membrane is pale and smooth, or detached in shreds; sometimes red, with the black veins strongly marked and corrugated. While deep erosions are not uncommon, it is rare to have complete solution of the walls of the stomach, so as to cause the symptoms of perforation during life, Both peritonitis and pleuritis have been found as complications, and perforations of the stomach also, but these last in some cases have been supposed to be due to changes after death. The kidneys are congested and loaded with oxalates.

Tests.—A solution of oxalic acid or of potassium binoxalate reddens litmus-paper.

Calcium Test.—Either of them yields, with excess of calcium hydroxid, acetate, or sulphate, a white precipitate of calcium oxalate, insoluble in ammonia or acetic acid, but soluble in strong hydrochloric or nitric acid.

Silver Nitrate Test.—Either of them gives with silver nitrate a copious white precipitate of silver oxalate, soluble in ammonia and in nitric acid, while silver chlorid would be insoluble in the nitric acid. The silver oxalate, dried and heated on platinum, disperses with a slight explosion and a white smoke.

Lead Acetate Test.—With lead acetate a white precipitate of

lead oxalate is formed which is soluble in nitric acid, but insoluble in acetic acid.

Potassium Permanganate Test.—Mixed with potassium permanganate and dilute sulphuric acid the oxalic acid is oxidized ($H_2C_2O_4 + O = 2CO_2 + H_2O$), and the permanganate, slowly losing its color, is converted into manganese sulphate.

Sublimation Test.—Heated on platinum foil, the acid crystals slowly sublime at as low a temperature as 100° C. (212° F.), and they are entirely and promptly dissipated at 160° C. (302° F.). At this temperature a large part is decomposed, first into formic acid and carbon dioxid. Thus:

$$\underset{}{H_2C_2O_4} = \underset{\text{Formic acid.}}{H_2CO_2} + CO_2.$$

The rising temperature then decomposes the formic acid into carbon monoxid and water. Thus:

$$H_2CO_2 = CO + H_2O.$$

The potassium oxalate does not sublime, but changes to potassium carbonate, which effervesces when touched with an acid, and turns red litmus-paper blue.

$$\underset{\text{Potassium oxalate.}}{K_2C_2O_4} = \underset{\text{Potassium carbonate.}}{K_2CO_3} + \underset{\text{Carbon monoxid.}}{CO}$$

Detection.—The symptoms of corrosive poisoning from an acid liquid which has left no colored spots upon the skin would be significant. A strong solution makes on black cloth a dark-brown, uncorroded spot, which gives the oxalic acid reactions. The vomited matters should be searched for the leaves of sorrel or green material of the rhubarb pie; not that these are ever fatal, but so as to exclude the possibility of a complication in the analysis. In the vomited matters and gastric contents the acid will be partly free, partly combined as soluble oxalate, and partly combined as the insoluble calcium or magnesium oxalates. If it should be mostly free, the following method will serve:

1. Having made an extract with hot dilute hydrochloric acid and filtered it, add lead acetate, which will throw down the lead oxalate along with various other lead compounds. This deposit should be suspended in water and hydrogen sulphid passed through it for two hours. The oxalic acid is set free in solution, the black lead sulphid being thrown down. After separation by a filter the filtrate should be tested with calcium acetate.

2. If the oxalic acid is in the combined state, the following is the better method: Digest the suspected matters with warm

dilute hydrochloric acid until the mixture is quite fluid, filter, and to the filtrate add ammonium hydroxid until an alkaline reaction is reached. After standing the liquid is decanted and the deposit collected on a filter. This deposit is calcium oxalate. The filtrate mixed with the decanted fluid is treated with excess of calcium acetate and the precipitate separated on a filter. This second deposit represents the free acid in the original material. To determine the nature and amount of the first deposit, it should be washed with acetic acid on the filter and afterward put into a beaker and dissolved by cautiously adding strong hydrochloric acid and gently heating. Excess of ammonia will precipitate it completely if sufficient time is allowed. After decanting the clear fluid the deposit is washed by decantation, put into a tared dish, dried in a water-bath, and weighed. If this deposit is calcium oxalate, it will be white, and when a portion is heated on platinum, leave a gray ash of calcium carbonate. Another portion warmed in a test-tube with strong sulphuric acid evolves carbon dioxid gas, which can be identified by conducting it through a delivery tube into baryta water. A third portion, suspended in water slightly acidulated with sulphuric acid, will discharge the purple color of potassium permanganate. This test can be applied by standard volumetric solutions and an estimate of quantity obtained.

If the poison has been taken as neutral sodium or potassium oxalate, the local symptoms and pathologic changes may not be at all characteristic. The effects come on after absorption and are mainly systemic. To make a complete examination the poison must be looked for outside the alimentary canal, by separating it from the urine and the finely divided tissue of the kidney. The method would be the same as that for vomited matters containing the combined acid.

SILICON (Silex, a flint)

Symbol, Si. Atomic weight, 28.3.

Properties.—Silicon is a tetrad element like carbon, never found native, but combined with oxygen as silica, SiO_2. Silica exists nearly pure in rock crystal or quartz, in sand, flint, and many minerals, and is also found combined with the metals as silicates. Silicon, next to oxygen, is the most abundant element known. It resembles carbon in physical and chemical properties. Like carbon it has three modifications, viz.:

Amorphous—a brown powder, only acted upon by hydrofluoric acid, HF, which dissolves it.

Graphitoidal—hexagonal plates with metallic luster.

Adamantine—in steel-gray crystals, hard enough to scratch glass.

Silicic Anhydrid, Silicon Dioxid (SiO_2) (*Silica*).—**Properties.**—It is a snow-white, gritty, insoluble powder, almost infusible, but soluble in hydrofluoric acid, HF. It is prepared by heating metasilicic acid, H_2SiO_3:

$$H_2SiO_3 \quad + \quad \text{heat} \quad = \quad H_2O \quad + \quad SiO_2.$$

Silica also exists, in a crystallized form, as quartz. Joined to one or more molecules of water silica forms a series of acids, like the phosphoric acids, viz.:

Metasilicic acid, $SiO_2 + H_2O = H_2SiO_3$; and

Orthosilicic acid, $SiO_2 + 2H_2O = H_4SiO_4$.

Metasilicic acid (H_2SiO_3) is a clear limpid fluid, in a *colloidal* solution, with a tendency to become gelatinous. It is the chief agent in petrifaction. It is prepared by acting upon potassium silicate, K_2SiO_3, with hydrochloric acid, HCl. Thus:

$$K_2SiO_3 \quad + \quad 2HCl \quad = \quad 2KCl \quad + \quad H_2SiO_3.$$

Orthosilicic acid (H_4SiO_4) is a white gelatinous substance when first precipitated, and soluble until evaporated to dryness. It is prepared by leading silicon tetrafluorid, SiF_4, into water. Thus:

$$3SiF_4 \quad + \quad 4H_2O \quad = \quad 2H_2SiF_6 \quad + \quad H_4SiO_4.$$

Orthosilicic acid results, together with a new acid, H_2SiF_6, to which the name of *hydrofluosilicic acid* is given.

Most of the silicates found in nature are derived from metasilicic acid, H_2SiO_3, to which the normal or orthosilicic acid reverts when it is set free, H_4SiO_4 losing H_2O, becoming H_2SiO_3.

Glass.—Silicates of the alkaline metals are soluble, one of them, known as sodium *water-glass*, was official as *liquor sodii silicatis*. This is prepared by fusing together sand and dry sodium carbonate: $Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$. Dissolving in boiling water to make a thick liquid it can be used as a cement or artificial stone. It loses water rapidly and becomes a glass. When bandages and fracture dressings are covered with it they soon harden and make an immovable apparatus. To remove them hot water must be applied. It is no longer used for bandages.

Common glass is a silicate of calcium and sodium, lime being introduced with sodium carbonate to make the glass insoluble.

Hard German, or *Bohemian glass*, is made with sand, lime, and potassium carbonate. It stands heat better than the soft French glass, of which chemical apparatus is usually made.

Soft French glass is a silicate of calcium, sodium, and aluminium.

English flint glass, used for optical purposes and ornamental cut glassware, has the calcium replaced with lead. It is more fusible and has a higher refracting power for light rays.

Silicon hydrid (SiH_4) is a colorless gas, taking fire spontaneously in the air, forming water and white cloud rings of silica.

Silicon tetrafluorid (SiF_4) is a colorless, pungent gas, fuming in air, and is formed when hydrofluoric acid comes in contact with silica. It is prepared by heating fluorid of calcium with sand or silica and sulphuric acid:

$$2CaF_2 + SiO_2 + 2H_2SO_4 = 2CaSO_4 + 2H_2O + SiF_4.$$

It is decomposed by water, but may be collected over mercury, or by displacement. A corresponding compound with bromin is known, called *Silicon bromid*, $SiBr_4$.

Silicon tetrachlorid ($SiCl_4$) is a colorless, pungent, irritating liquid, formed when silicon is heated in chlorin.

Silicon resembles carbon in the composition of its salts. Thus:

CO_2	H_2CO_3	CH_4	CCl_4.
SiO_2	H_2SiO_3	SiH_4	$SiCl_4$.

But the two elements also differ widely in some respects. While both form many compounds, the carbon derivatives have a structure showing very different relationships to the carbon from those of the silicon derivatives to the silicon. Carbon compounds appear to be derived from the hydrocarbons; silicon compounds arise from or are related to silicon dioxid.

Carborundum.—At the very high temperature of 3500° C. obtained in an electric furnace, the following reaction occurs in a mixture of carbon, sand, and salt:

$$SiO_2 + 3C = SiC + 2CO.$$

The greenish-black mass SiC is called technically "carborundum." It is used as a grinding material, being of sufficient hardness to replace the diamond in glass cutting. It resists the strongest acids, but decomposes by fusion with alkalis.

"Weathering" of Rocks.—It is a remarkable fact that the stable and insoluble silicates in granite and other primitive rocks when exposed to the air break up into loose soil and soluble carbonates, by displacement of the silicic acid in their constituents with the carbonic acid of the air. This result of weathering makes resistant minerals turn to sources of fertility, as the alkaline carbonates thus liberated are necessary to plants. A process imperceptible in any laboratory experiment, with the small mass of carbonic acid ordinarily engaged, becomes on the large scale of nature and in geologic time a reaction of great importance, owing to the enormous quantities of carbonic acid in the air and surface waters unceasingly at work.

BORON

Symbol, *B*. Atomic weight, 11.

Properties.—Boron is a triad element which is never native, but is found united with oxygen and sodium as borax; and with oxygen alone as boron trioxid. It occurs in three modifications:

Amorphous boron—a dull gray powder which, when strongly heated in air, burns to boric oxid, B_2O_3.

Graphitoidal boron, in scales with graphite-like luster.

Diamond boron is square octahedra of cupreous luster; hard enough to scratch a ruby.

Boron, when heated strongly in chlorin or oxygen, takes fire, forming a chlorid or oxid. It is remarkable as being one of the few elements uniting directly with nitrogen, which gas it absorbs when red hot with the evolution of light, forming boron nitrid, BN. Boron with chlorin forms a liquid called boron trichlorid, BCl_3; with hydrogen a trihydrid, BH_3.

Boron Trioxid, Boric Anhydrid (B_2O_3).—This compound fuses to a glass, which retains its clearness on cooling. It is prepared by heating boric acid, H_3BO_3:

$$2H_3BO_3 = 3H_2O + B_2O_3.$$

By reversing the reaction with water B_2O_3 forms *boric* or *boracic acid*, H_3BO_3 (Acidum Boricum, U. S. P.).

Boric acid is a tribasic weak acid, crystallizing in pearly plates from a hot solution as it cools. It is found in the fumerolles (steam jets) which are constantly escaping from the earth in old volcanic districts of Tuscany, and in the lagoons which collect at the mouth of these jets. The boric acid is concentrated by the heat of the natural steam jets, and is finally obtained pure by crystallization. *Sodium borate* also occurs in California and Thibet.

Preparation.—Boric acid may be prepared by the action of hydrochloric acid on a hot solution of borax, $Na_2B_4O_7$:

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3.$$

A 10 per cent. ointment is official.

Borax is the salt most largely used in the arts; it is Sodii Boras, U. S. P.

Borax ($Na_2B_4O_710H_2O$) (*Biborate of Soda*).—This substance is a native salt, but can be artificially prepared by heating together boric acid and sodium carbonate:

$$4H_3BO_3 + Na_2CO_3 = 6H_2O + CO_2 + Na_2B_4O_7.$$

Borax is a salt of a tetraboric acid, formed from the normal acid, H_3BO_3, by loss of water. Thus: $4H_3BO_3$ deprived of $5H_2O$ yields $H_2B_4O_7$. Borax is much used as a blow-pipe reagent in the laboratory, since many metallic oxids are soluble in fused borax, yielding colored glasses. It is also used as a flux to clean metals when they are to be soldered with hard solder.

Its solution has an alkaline reaction and is largely used in medicine locally to destroy bacteria.

Liquor antisepticus (U. S. P.) is a solution of boric acid, benzoic acid, and thymol in a diluted tincture of antiseptic aromatics.

Toxicology of Boric Acid and Borax.—The local effect of boric acid being very mild, its virtues as a bactericide have led to its use in surgical practice, especially for washing out cavities and sinuses to prevent septic changes. Cases are recorded of depression and eruptions of erythema and urticaria following its absorption from wounds and cavities when used too freely. Occasionally, graver phenomena have appeared, such as vomiting, diarrhea, bloody urine, and collapse. Fatal results have ensued in a few cases from injecting the solution into the abscess sacs and from washing out the stomach with it.

The toxicology of boric acid and borax is limited practically to the use of these agents as preservatives of food. They destroy the germs of fermentation and putrefaction in solid and liquid foods. For meats they have been mixed with salicylic acid and applied externally. For preserving milk it was once a common practice to add to 1 qt. of milk 10 gr. of a mixture of equal parts of borax and boric acid.

Experiments upon men, conducted by the U. S. Agricultural Bureau, proved that "both boric acid and borax, when continuously administered in small doses for a long period, or when given in large quantities for a short period, create disturbances of appetite, of digestion, and of health." Even in the small amounts required for preserving cream and butter, and that used as an external dust on hams and bacon, which have to be transported long distances, both boric acid and borax are objectionable from a sanitary standpoint. Such food substances should be frankly labeled as *preserved* by the addition of borax and boric acid.

As these substances are not normal constituents of the body, it is best to avoid their use, since the most conclusive evidence has been adduced that they are not free from harm in the amounts as commonly used for preserving food.

Detection of Boric Acid in Meat.—*Jorgensen's test* makes use of the property of neutralized boric acid to take on an acid reaction after treatment with glycerin. The meat is made strongly alkaline with sodium hydroxid, extracted with hot water for several hours,

and the extract filtered. The filtrate is evaporated to dryness, incinerated, and the ash dissolved in sulphuric acid, by warming the carbon dioxid is removed, and on cooling the solution is neutralized by an alkaline hydroxid, using phenolphthalein as indicator.

To 50 c.c. of the neutral fluid 25 c.c. of glycerin are added, and the mixture titrated with decinormal sodium hydroxid solution without regard to the phosphates. The end-reaction is made more definite by the addition of ethyl alcohol.

Detection in Milk.—*Turmeric Test.*—Place in a porcelain dish 1 drop of the milk with 2 drops of strong hydrochloric acid and 2 drops of a saturated turmeric tincture. Dry this on a water-bath, cool, and add a drop of ammonia by means of a glass rod. A slaty-blue color changing to green is produced if borax is present. A drop of milk containing $\frac{1}{1000}$ gr. of borax will give this reaction.

Flame Test.—With alcohol boric acid forms a volatile ester which burns with a *green* flame. Material suspected of containing boric acid is put in a capsule and covered with sulphuric acid. Alcohol is poured over the mixture, which is heated until it takes fire. The green color of the flame is very characteristic.

THE METALS

The metals are easily recognized by properties common to all and illustrated in well-known examples, such as gold, silver, copper, and lead. All except mercury are solid at ordinary temperature. They conduct well both heat and electricity, and many can be polished so as to reflect light, this quality being described as *metallic luster.* Most of them are dense and heavy, can be drawn into wires (*ductile*), hammered into thin plates (*malleable*), and resist attempts to break them (*tenacious*). All are opaque except when reduced to the thinnest films, such as gold-leaf. When metals combine among themselves they make *alloys;* if the union be with mercury, it is called an *amalgam.* These combinations are not attended by loss of metallic character.

When solutions of metallic salts are put in electrolytic cells the metals invariably seek the negative pole, and hence are *cations.*

In the present work a classification is adopted deemed suitable for the needs of the medical student. The resemblances which are emphasized and which form the basis of the groups are such as have significance growing out of their medical or toxic relations. Several very different arrangements are possible, which might be regarded as more suggestive and more helpful to the

non-medical students of chemistry, because they include a greater number of analogies. One of these is the natural system referred to on p. 116.

The important metals will be considered in the order of the following groups, the lightest metals presenting the highest powers of uniting with oxygen:

<table>
<tr><td>I. Alkali metals: oxids and most salts soluble.</td><td rowspan="3">Light metals with specific gravity not exceeding 4. Sulphids soluble in water.</td></tr>
<tr><td>II. Alkaline earth metals: oxids soluble, carbonates insoluble.</td></tr>
<tr><td>III. Earth metals: oxids insoluble.</td></tr>
<tr><td>IV. Arsenic group: sulphids insoluble in dilute acids, but soluble in ammonium sulphid.</td><td rowspan="4">Heavy metals with specific gravity exceeding 4. Sulphids insoluble in water.</td></tr>
<tr><td>V. Copper group: sulphids insoluble in dilute acids, and in ammonium sulphid.</td></tr>
<tr><td>VI. Iron group: sulphids soluble in dilute acids.</td></tr>
<tr><td>VII. Gold group: sulphids insoluble in dilute acids, but soluble in ammonium sulphid.</td></tr>
</table>

THE LIGHT METALS

I.—THE METALS OF THE ALKALIS

Potassium, K.	Ammonium, NH_4, hypothetic.
Sodium, Na.	Cesium, Cs.
Lithium, Li.	Rubidium, Rb.

The members of this group are all univalent, some of them are lighter than water, and nearly all of their compounds are soluble in water. They never occur free in nature, because of their great power of forming compounds. This also makes it necessary to resort to unusual precautions to protect them from such union. Their oxids, hydroxids, and carbonates are alkaline in reaction. None of the group reagents has any visible effect upon solutions of the salts belonging to this group. Their chlorids and sulphids are all soluble and, therefore, are not precipitated by hydrochloric acid, hydrogen sulphid, or ammonium sulphid. Unlike the alkaline earths, they (except lithium) are not precipitated by ammonium carbonate.

Corrosive Alkalies.—Under this heading will be considered the hydroxids or hydrates of potassium, sodium, and ammonium. It is well to note that their basic *carbonates* also are not only strongly alkaline in reaction, but in concentrated solution have a corrosive effect. The action of the corrosive alkalies is chemical or local, and limited to the part with which they come in contact. This corrosive power is due to their solvent action on albumin, their saponifying property when mixed with fatty matter, and their avidity for the water of the tissues. They cause rapid and deep destruction of the animal structures. The local symptoms are

like those of corrosive acids. The general symptoms are likewise those of the shock of a violent lesion added to the immediate consequences of the lesion due to its locality. Poisoning from them is most often accidental, though they are not infrequently taken with suicidal intent.

POTASSIUM (Kalium)

Symbol, K. Atomic weight, 39.10.

Occurrence.—Potassium is found in nature in its compounds only. Among these are *saltpeter*, *feldspar*, and *carnallite*. The disintegration of feldspar by the weather furnishes the soil with potash in a form assimilable by plants, required by them for their growth, they in turn furnishing it in vegetable food to animals. In small quantities potassium is indispensable to the animal organism, being a constituent of the red blood-corpuscles. When greatly concentrated many of its salts act as irritants or corrosives. Even if diluted, the continuous administration of these salts in full doses brings about anemia, loss of energy, and other indications of impaired nutrition. This toxic action is attributable to the potassium ion in the blood in excess of the physiologic need.

The ashes of wood, leached with water, yield potassium carbonate; the water evaporated by boiling leaves crude potash, formerly the chief source of the other compounds.

Preparation.—Potassium is now prepared by electrolysis of the fused hydroxid or chlorid, $K^{\cdot},Cl'=K+Cl$. The older chemical method was to heat potassium carbonate with charcoal. The carbonate yields oxygen to the reducing carbon to form the gas carbon monoxid, and the metal is vaporized to condense under petroleum. Thus:

$$K_2CO_3 \quad + \quad 2C \quad = \quad 2K \quad + \quad 3CO.$$

Properties.—Freshly cut surfaces of potassium show a silver-white luster. At ordinary temperatures it is soft, like wax, and can be molded by the fingers. At a red heat it passes into a blue-green vapor. It combines with oxygen with so much velocity that it decomposes water violently, and, exposed to the air, tarnishes immediately. For protection potassium must be kept under petroleum or in hydrogen gas. In time, even in coal-oil, it unites with some dissolved oxygen and becomes covered with a gray-brown crust, which, however, shields the deeper parts.

Potassium Dioxid (KO_2).—This is prepared by heating potassium in oxygen. It is an orange-colored powder used to form hydrogen dioxid.

$$2KO_2 \quad + \quad 2H_2O \quad = \quad 2KOH \quad + \quad H_2O_2 \quad + \quad O_2.$$

Potassium Hydroxid (KOH) (*Potassium Hydrate, Caustic Potash*).—**Preparation.**—When thrown upon water, a piece of potassium floats about on the surface, melts, forms a silvery ball, bursts into a reddish-violet flame, and grows red hot. As the metal is consumed the flame goes out, the incandescent ball of hydroxid cools down to the point when wetting is possible, and then dissolves with such a sudden evolution of heat that a steam

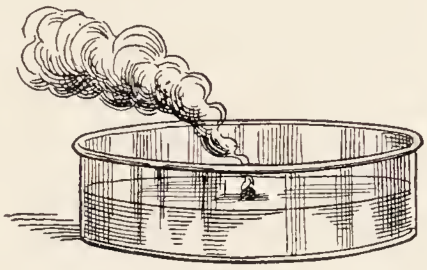


FIG. 59.—Potassium decomposing water.

explosion occurs. The violet or lavender flame is hydrogen ignited by the heat of chemical action and colored by particles of potassium (Fig. 59).

$$H_2O \quad + \quad K \quad = \quad KOH \quad + \quad H.$$

Commercially it is manufactured by first electrolyzing potassium chlorid, using a cathode of mercury. The mercury makes an amalgam with the potassium, and the amalgam, in contact with water, forms the hydroxid, the free mercury being again ready for use as a cathode.

If mercury be not used as a cathode, the movement of the ions occurs in the sense of the following equation:

$$K^+, Cl^- \; + \; H^+, (OH)^- \; = \; H \; + \; Cl \; + \; K^+, (OH)^-.$$

The chlorin ions give up their charge at the anode and escape as gas. The potassium ions seek the cathode with a strong charge; there they find some of the weakly dissociated hydrogen ions of the water, which discharge upon the cathode and are set free as gas. The remaining hydroxyl anions are held in relation to the potassium cations as potassium hydroxid in solution.

The older method of preparation was to decompose potassium carbonate with calcium hydroxid in weak solution. The reaction is expressed thus:

$$K_2CO_3 \quad + \quad Ca(HO)_2 \quad = \quad CaCO_3 \quad + \quad 2KOH.$$

The calcium carbonate is precipitated, and the potassium hydroxid is separated by boiling off the water of the filtered solution.

Properties.—The pure substance is a gray-white solid with an angular fracture. It imparts a soapy feeling when handled, has a soapy taste, and a strong alkaline reaction to litmus. Heated, it melts to a colorless liquid; run into cylindric molds it makes *potassa fusa*, the ordinary form seen in shops. It dissolves in half its weight of water, evolving heat; it is soluble also in alcohol and glycerin, but insoluble in ether. It deliquesces rapidly, and in the moist state freely takes up carbon dioxid gas to make potassium carbonate. It is a typical base, dissociating strongly and developing in a high degree the alkaline properties of hydroxidion. A very small quantity in solution makes litmus blue and phenolphthalein red.

Pharmaceutic Preparation.—*Potassii hydroxidum* occurs in cylindric rods. *Liquor potassii hydroxidi* (U. S. P.) is a colorless, acrid, alkaline, corrosive liquid with a specific gravity of 1.036, and containing about 5 per cent. of potassium hydroxid. *Potassa cum calce* (Vienna paste) is made of equal parts of potassa and quicklime. The two carbonates resemble the hydroxid in toxic effects, but differ in degree. *Potassii carbonas impura* (pearl-ash), under the name of potashes, used for cleansing oil-lamps, occurs as a dark mass, deliquescent, strongly alkaline, and caustic. *Potassii carbonas pura* occurs as white crystals, deliquescent, alkaline, and caustic.

Symptoms.—Taken in strong solution, a large dose of caustic potash or the carbonate will cause a nauseous, soapy taste, accompanied by burning pain in the mouth, throat, and stomach. Vomiting of alkaline bloody material soon follows, and later colicky pains and great abdominal tenderness with purging of shreds of epithelium, mucus, and blood. The lips and tongue swell and turn brown, swallowing is difficult, and the skin cold and damp, the breathing hurried and shallow. Surviving these symptoms, the patient may die after some days of starvation from stricture of the gullet.

Fatal Dose.—The ordinary fatal quantity is $\frac{1}{2}$ oz. (15.5 gm.), but 30 gr. (2 gm.) have proved sufficient.

Fatal Period.—From the acute effects death may come in three hours; from the secondary effects the final event may be delayed for weeks or even years. The average duration is about twenty-four hours.

Treatment.—The local action of the poison should be lessened by copious drafts of water, alone or acidulated. The chemical antidotes are weak acids and oils. The most convenient weak acid is vinegar, but diluted lemon-juice or orange-juice will serve. Milk, olive oil, melted butter, or lard would also neutralize the alkalis, though not so promptly. The stomach-pump is not admis-

sible. The pain will call for morphin injections; collapse should be met by stimulants, and threatened starvation by nutritive enemata.

Postmortem Appearances.—The mouth, throat, and gullet are whitish and softened. The stomach and intestines are bright red or black from extravasated blood; the lining membrane disorganized and stripped in patches. The secondary pathologic changes seen when death closes the history of a chronic case are denudation of the lining membrane, ulceration, and points of stricture in gullet or pylorus.

Detection.—As alkalinity of the gastric contents has never been reported in any normal case, the mere fact that vomited matters or gastric contents have an alkaline reaction would be so exceptional as to be suspicious. After separating the soluble alkali from the undissolved matter by dialysis, the clear liquid should be titrated with decinormal sulphuric acid and tested for potassium (see p. 222). As the chlorid, sulphate, and phosphate of the metal are natural constituents of the food and of the body itself, more or less of these will be found always present. Hence if the fluid is not alkaline, the process must include quantitative determinations of the different metals. If the analyst can obtain a sample of the substance taken or a piece of the clothing stained, his task is much simpler.

Potassium chlorid (KCl) is found in Germany in the mineral *carnallite*. It is a double chlorid of magnesium and potassium. To obtain the potassium chlorid from this mineral a hot solution is made, which on cooling separates the potassium chlorid as crystals.

Properties.—Potassium chlorid forms white cubic crystals much more soluble in hot water than in cold. It is typical of the salts formed by a strong acid, HCl, acting on a strong base, KHO, and in solution its ions are completely dissociated.

Potassium bromid, KBr, can be formed, as other bromids, by the direct action of bromin on the metal, though the more convenient method is action on the hydroxid:

$$6KOH + 6Br = 5KBr + KBrO_3 + 3H_2O.$$

Properties.—It crystallizes in white cubes without odor, but with a salty and nutty taste. It is soluble in about 2 parts of water, 4 of glycerin, but requires 200 of alcohol. Its solution is a convenient source of bromin ions. Dose: 15 to 60 gr. (1–4 gm.), repeated. If long continued, there is danger of inducing *bromism* (see p. 144). It is incompatible with acids, alkaloids, and the salts of silver, mercury, lead, copper, bismuth, and antimony.

Potassium iodid, KI, is prepared by a reaction between potassium hydroxid and ferrous iodid:

$$FeI_2 + 2KOH = Fe(OH)_2 + 2KI.$$

The ferrous hydroxid is precipitated, the potassium iodid remains in the filtrate.

Properties.—It occurs in white cubes of a bitter, salty taste, soluble, 1.27 parts in 1 of water, in glycerin 1 part to 3, in alcohol 1 to 18. Dose: 3 to 30 gr. (0.19–1.9 gm.), repeated. Care should be observed lest *iodism* be induced (see p. 147). The ion of iodin is well represented in the aqueous solution. It is incompatible with acids, metallic salts (especially silver nitrate, calomel, and potassium chlorate), chloral hydrate, and salts of alkaloids.

Potassium chlorate ($KClO_3$) is obtained when chlorin acts on potassium hydroxid:

$$6KOH + 6Cl = 5KCl + KClO_3 + 3H_2O.$$

Of the two salts the chlorate is less soluble, and on evaporation of the mixed solution it crystallizes first.

Properties.—Its crystals are beautiful white plates with a cool saline taste, soluble in about 17 parts of water, insoluble in alcohol. In the laboratory it is chiefly valuable as a store of oxygen, which it readily yields on heating. Dose: 10 to 20 gr. (0.64–1.29 gm.), diluted, after meals. Tablets for sore mouth, 5 gr. each. It is incompatible with tartaric acid and ferrous iodid. It is likely to explode when rubbed in a mortar with sugar, sulphur, or phosphorus.

This salt is much used in the manufacture of explosives and flashing powders, and in medicine. In the household it is a common remedy for sore mouth and throat, and through a belief in its harmlessness, often leads to injury.

Symptoms.—If used as a mouth-wash it is harmless, but when swallowed in large doses it is irritant, causing abdominal pain, vomiting, diarrhea, and even collapse. A case of poisoning has been reported from two teaspoonfuls taken in two days for sore throat. It caused violent intestinal irritation, with black stools, considerable urinary disturbance, with black urine, great prostration, and evidences of grave alteration of the blood.

When absorbed, it has a peculiar destructive action on the red corpuscles of the blood, converting the hemoglobin into methemoglobin and setting up secondary symptoms, such as jaundice, hemoglobinuria, suppression of urine, bloody tube-casts, delirium, coma, and death as a consequence of the acute nephritis.

Fatal Dose and Period.—Forty-six grains (2.9 gm.) proved a fatal dose in a child three years old. The minimum adult dose reported as fatal is 3 dr. (11.65 gm.). Fountain took $1\frac{1}{8}$ oz. with fatal consequences in seven days. If a certain amount is given in divided doses, the effect is more severe than when given in a single dose. Death has occurred in five hours, but usually it results from nephritis after several days.

Treatment.—Having washed out the stomach with the tube or pump, the secondary effects must be combated with appropriate remedies. The kidney complications will require active local treatment.

Postmortem Appearances.—The marks of gastro-enteritis will be found—*i. e.*, a mucous membrane reddened, thickened, and easily detached. Inflammatory changes are seen in the spleen, liver, and especially in the kidneys. These organs are enlarged and dark brown in color, from the presence of the altered hemoglobin.

Detection.—As the salt is unchanged in the body, it can easily be separated from organic matter by dialysis. Having colored the suspected solution with indigo sulphate and acidulated with dilute sulphuric acid, the addition of sulphurous acid will discharge the blue color if the chlorate be present.

Potassium nitrate (KNO_3) (*saltpeter, niter*) is found in the soil of India and can be procured by leaching with water. It is also formed artificially in "plantations" of bacteria. Nitrogenous waste of animals mixed with the potassium carbonate of wood ashes make a soil for the growth of the nitrifying bacteria. These ferments cause the ammonia of putrefaction to be oxidized to nitric acid, which unites with the potassium of the wood ashes to form KNO_3. After several years the fermenting material is leached and the crude nitrate dissolves out, to be purified by crystallization. Like the chlorate, this salt is a liberal oxidizer.

The chief source now is double decomposition of "Chili saltpeter," sodium nitrate, and potassium chlorid:

$$NaNO_3 + KCl = KNO_3 + NaCl.$$

Hot saturated solutions are used which retain KNO_3, but separate the less soluble NaCl. This leaves a liquid which on cooling yields crystals of KNO_3.

In 100 parts of gunpowder there are of KNO_3 75 parts; sulphur, 12 parts; carbon, 13 parts. Owing to the intimacy of the mixture, combustion is immediate and complete.

Properties.—It forms large hexagonal prisms, permanent in the air. Without odor, they have a cool saline taste, and are soluble in 4 parts of water. Dose: 10 to 60 gr. (0.65–4 gm.).

Under the name *sal prunelle* potassium nitrate is found to be molded in small balls. It is used as a remedy for the diseases of cattle; also in the preservation of the original reddish color of salted meat and in the manufacture of explosives. In the crystalline form it has been taken as a purgative by mistake for magnesium sulphate in 8 cases. In 2 cases it has been mistaken for common salt.

Symptoms.—While doses of 1 dr. (4 gm.) cause minor degrees of gastric and intestinal irritation. doses of from $\frac{1}{2}$ to 1 oz. (16–32 gm.) excite acute gastro-enteritis. There are vomiting, abdominal pain, diarrhea, perhaps bloody in character, localized muscular spasms, disturbed respiration and heart action, and collapse.

Fatal Dose.—Though an adult has died from the effects of 2 dr., other cases have recovered from a dose of 1 oz.

Fatal Period.—Two hours is the shortest period in which death has taken place; the average duration of fatal cases is somewhat longer.

Treatment.—The stomach must be evacuated by emetics, and the stomach-pump or tube used to wash out the poison. Bland demulcents may be administered, and the tendency to collapse overcome by stimulants and warm applications.

Detection.—As nitrates are not present in the body, the presence of a notable quantity in the gastric contents or other organic mixture would be significant. By adding sulphuric acid the nitric acid is freed and the tests for the acid can be applied (see p. 172).

Copper Tests.—Heated in a test-tube with sulphuric acid and copper turnings, nitrates evolve red fumes of nitrogen oxids.

Brucin Test.—Mixed with an equal volume of sulphuric acid, a nitrate solution produces a tint of carmin on the addition of a trace of brucin.

Potassium Nitrite (KNO_2, H_2O).—This is formed when part of the oxygen of potassium nitrate is liberated by heating:

$$2KNO_3 = 2KNO_2 + O_2.$$

When the nitrate is employed to oxidize metals, such as lead, the nitrite is also obtained as the reduced salt:

$$KNO_3 + Pb = KNO_2 + PbO.$$

The aqueous solution of this salt of a weak acid is alkaline from the preponderance of hydroxyl ions caused by the hydrolysis, the acid being almost undissociated:

$$K^+, (NO_2)^- + H_2O = K^+, (OH)^- + HNO_2.$$

The nitrous acid, HNO_2, is set free in solution when sulphuric acid is added to a solution of potassium nitrite. Its anhydrid is N_2O_3.

Potassium hydrosulphid, KHS, is formed by saturating a solution of potassium hydroxid with the gas hydrogen sulphid:

$$KOH + H_2S = H_2O + KHS.$$

As a salt of sulphydric acid, which is weak in its acid properties, hydrolytic dissociation occurs, forming hydroxidion in amounts dominating the hydrion, which is scarcely dissociated from the acid, and, therefore, making an alkaline solution. Thus:

$$K^+, (HS)^- + H_2O = K^+, (HO)^- + H^+, (HS)^-.$$

Potassium monosulphid, K_2S, as a hydrolyzed alkaline solution, is obtained by adding potassium hydroxid to potassium hydrosulphid:

$$KHS + KOH = K_2S + H_2O.$$

Four other sulphids are known, the higher polysulphids being interesting as components of the medicinal compound. *Potassii sulphuratum*, *hepar sulphuris*, or *liver of sulphur*, is the product obtained by fusing together potassium carbonate and sulphur. It is a brownish-yellow mixture of sulphids, varying in composition between the trisulphid, K_2S_3, and the pentasulphid, K_2S_5. Dose: ½ to 5 gr. (0.03–0.3 gm.).

Potassium sulphate, K_2SO_4, occurs in combination with magnesium chlorid in the mineral *kainite*, and also in mineral waters. Its hard prismatic crystals have a bitter, salty taste, are permanent in the air, and are soluble in 10 parts of water. It is a laxative in doses of 15 to 75 gr. (1–5 gm.) in solution. In excessive doses it has proved poisonous, causing abdominal pain, vomiting, purging, exhaustion, and fatal collapse. There is no specific antidote. The stomach should be evacuated and the irritation and depression treated as they arise.

Potassium Acid Sulphate, or *Potassium Bisulphate* ($KHSO_4$).—This is obtained as a by-product in the manufacture of nitric acid. It is formed when the normal sulphate is treated with more sulphuric acid; hence the name *bisulphate*.

$$K_2SO_4 + H_2SO_4 = 2KHSO_4.$$

Its colorless, moist plates are freely soluble in water, making a strongly acid solution. This reaction is caused by the strong

acid, H_2SO_4, dissociating to a slight extent its unreplaced hydrogen. Thus:

$$KHSO_4 = K^+, H^+, (SO_4)^=.$$

Potassium bisulphate is used in medicine as an aperient tonic. Dose: 60 to 120 gr. (3–5 gm.).

Potassium Sulphite (K_2SO_3).—This is formed by saturating with sulphur dioxid a solution of potassium carbonate or hydroxid. Evaporating the solution over sulphuric acid, the sulphite is obtained crystallized in rhombohedra. These crystals are soluble in water, and in solution change to K_2SO_4 by absorbing oxygen from the air. The *pyrosulphite*, $K_2S_2O_5$, oxidizes very slowly in air and is employed in photography. In water it makes an acid-sulphite solution containing the ions K^+ and $(HSO_3)^-$.

Potassium carbonate, K_2CO_3, occurs in the animal body and in mineral waters. For many years it was produced by leaching with water the ashes of plants, and then boiling off the water. The *impure potash* or *pearlash* was purified by solutions and crystallizations, so as to make *pure* potassium carbonate. The modern method of preparation is to electrolyze potassium chlorid; the hydroxid forming in the liquid around the cathode. Carbon dioxid is passed into the hydroxid solution, forming potassium carbonate.

Properties.—It is a white granular powder, deliquescent and remarkably soluble in water. At low temperatures, by evaporation, a salt crystallizes with the formula $2K_2CO_3, 3H_2O$.

Owing to the weakness of carbonic acid, there is an interchange with the ions of water which dissociates a sufficient percentage of free hydroxyl ions to cause a strong alkaline reaction. The hydrolysis is in accordance with this equation:

$$K^+, K^+, (CO_3)^= + H_2O = K^+, (OH)^- + K^+, (HCO_3)^-.$$

Owing to its caustic action, potassium carbonate is not given internally, but in dilute solution is used externally. (See Toxicology of Potassium Hydroxid, p. 214).

Potassium Acid Carbonate or *Potassium Bicarbonate* ($KHCO_3$).—This is obtained by saturating with carbon dioxid a solution of the normal salt:

$$K_2CO_3 + CO_2 + H_2O = 2KHCO_3.$$

In this operation the carbonate seems to take up another molecule of carbonic acid, H_2CO_3, and hence the name bicarbonate. On evaporation it crystallizes in rhombic prisms, much less soluble

than the carbonate, and almost insoluble in alcohol. The dilute aqueous solution is alkaline in taste and in reaction, in spite of the unreplaced hydrogen. This is explained by the hydrolysis converting the anion $(HCO_3)^-$ into undissociated H_2CO_3, and setting free a few ions of hydroxyl:

$$KHCO_3 + H_2O = K^+, (HO)^- + H_2CO_3.$$

Saleratus is a name given to the bicarbonate because when heated it yields CO_2, the aerating gas of "soda biscuits":

$$2KHCO_3 = K_2CO_3 + H_2O + CO_2.$$

If not used with other chemicals in yeast powders the residue in the bread is potassium carbonate, K_2CO_3, unwholesome because it irritates the stomach.

It is used in medicine as an antacid and antilithic. Dose: 20 to 60 gr. (1.3–4 gm.). Owing to its nauseous taste it is taken in an effervescent draught.

Potassium citrate, $K_3C_6H_5O_7.H_2O$, is a white, granular deliquescent powder having a cool salty taste; it is soluble in an equal weight of water, and slightly soluble in alcohol. The solution is neutral or feebly alkaline. Dose: 10 to 30 gr. (0.6–2 gm.).

Liquor potassii citratis is a palatable preparation in which the alkaline taste of the salt is overcome by the more agreeable flavor of citric and carbonic acids. It is prepared by dissolving 8 parts of potassium bicarbonate in 50 of water, and 6 parts of citric acid in another 50 of water and mixing the two solutions. It is a febrifuge and diuretic. Dose: ½ to 1 fl. oz. (15–30 c.c.).

Mistura potassii citratis (*neutral mixture*) is an agreeable preparation of potassium citrate made freshly by adding to 100 parts of fresh lemon juice about 10 parts of potassium bicarbonate to neutralize the citric acid of the lemon juice. Dose: same as for liquor potassii citratis. The neutral potassium salts of the carbon acids, citric, acetic, and tartaric, are converted into alkaline carbonates, either in the blood or the intestines, and when eliminated by the urine give it an alkaline reaction.

Potassii citras effervescens is a granular solid, containing 20 per cent. of potassium citrate mixed with enough sodium bicarbonate with tartaric and citric acids to react when dissolved with disengagement of carbon dioxid and forming soluble neutral salts.

Potassium acetate, $KC_2H_3O_2$, is prepared by neutralizing acetic acid with potassium carbonate or bicarbonate. This is obtained as white crystals, or as granular powder, very deliquescent,

and having a saline taste. They are neutral or freely alkaline in reaction, and feebly soluble in water and alcohol. Dose: 5 to 60 gr. (0.3–4 gm.).

Potassium tartrate ($K_2C_4H_4O_6$) (*neutral tartrate* or *dipotassic tartrate*), is made by neutralizing the bitartrate with potassium carbonate. It is obtained in small white crystals or powder, deliquescent, of saline taste, freely soluble in water, giving a neutral reaction; it is almost insoluble in alcohol. Dose: ½ to 4 dr. (2–16 gm.).

Potassium Bitartrate ($KHC_4H_4O_6$) (*Acid Tartrate, Cream of Tartar, Monopotassium Tartrate*).—This is produced in the course of fermentation of grape juice. The alcohol precipitates impure or *crude tartar*, the *argol* of commerce. Dissolved in boiling water, decolorized and washed in hydrochloric acid, it is crystallized by evaporation into colorless rhombs, having a sour taste, soluble in 200 parts of water and 15 of boiling water, and almost insoluble in alcohol. Dose: 1 to 4 dr. (4–16 gm.). In ordinary doses diuretic and laxative; in excessive doses an irritant poison, causing gastric pain, vomiting, diarrhea, and collapse. There is no specific antidote; emetics followed by soothing remedies are always called for.

Tests for Potassium Salts.—The detection of potassium K^+, depends upon its compounds of slight solubility formed with the anions of tartaric acid $(HC_4H_4O_6)^-$; of hydrochlorplatinic acid $(PtCl_6)^=$ of hydrofluosilicic acid $(SiF_6)^=$; of perchloric acid $(ClO_4)^-$; and the cobalt nitrite ion, $Co(NO_2)_6^{\equiv}$.

1. To a concentrated solution of a neutral potassium salt add a fresh strong solution of tartaric acid. The difficultly soluble bitartrate is precipitated white, more copiously if alcohol be added.

2. Acidulate the potassium solution with a few drops of hydrochloric acid and add platinum chlorid and alcohol. Yellow crystals of potassioplatinic chlorid form:

$$2KCl + H_2PtCl_6 = K_2PtCl_6 + 2HCl.$$

3. With potassium salts hydrofluosilicic acid slowly forms a translucent gelatinous precipitate, soluble in strong alkalies.

4. Perchloric acid yields a white precipitate, insoluble in alcohol.

5. With a neutral or slightly acid potassium solution, sodium cobaltinitrite gives the yellow precipitate of potassium cobaltinitrite: $(KNO_2)_6\,Co(NO_2)_6 + H_2O$.

6. The readiest test is the lavender or reddish-violet color imparted to a Bunsen flame. As sodium is often present and gives a yellow color, which masks the potassium violet, it may be nec-

essary to eliminate the yellow by viewing the flame through cobalt-blue glass. This permits the potassium light only to pass through, appearing reddish in color. Viewed by the spectroscope the lavender flame is resolved into a dull-red band and a faint violet line (Fig. 19).

SODIUM

Symbol, Na. Atomic weight, 23.

Occurrence.—Like the other alkaline metals, sodium is never found free in nature. If liberated and not protected, its activity causes it at once to unite with other elements. Its compounds, especially sodium chlorid, are very abundant and very soluble; hence, they are washed from many sources in large amounts by the waters flowing into the sea and lakes that have no outlet. Solid salt beds mark the place where salt lakes have evaporated. The vapors rising from the sea are borne inland, carrying into the air minute quantities of sodium chlorid. The sensitive spectroscope shows the bright-yellow sodium line in almost every observation, no matter what substance be examined.

Preparation.—At one time the metal was obtained by distillation of the carbonate by means of heated carbon:

$$Na_2CO_3 \quad + \quad 2C \quad = \quad Na_2 \quad + \quad 3CO.$$

But the most economic process is based upon the principle used by Davy when he first liberated it from the hydroxid by electrolysis. The electric current, generated by water power, is passed through fused sodium hydroxid, NaHO. At the cathode sodium and free hydrogen appear, the sodium, floating upon the hydroxid, is skimmed off; the oxygen escapes at the anode.

Properties.—Metallic sodium is a soft plastic solid, its freshly cut surface shining with a silvery luster, which soon tarnishes in the air. To protect sodium from the oxygen of the air it is kept under petroleum, but a more volatile hydrocarbon, like benzine, is preferred, as it is more easily removed from the surface of the metal. Like potassium (though it is less violent) it has an energetic reaction with water:

$$Na \quad + \quad H_2O \quad = \quad NaOH \quad + \quad H.$$

Thrown upon water, its movements are so vivacious as to dissipate its heat to a point below that which ignites hydrogen. If filter paper be floated on the water and a small piece of sodium placed upon it, the hot globule formed cannot move, and so enough heat is retained to set fire to the evolved hydrogen. The sodium gives the characteristic yellow color to the hydrogen flame,

and the hydroxid dissolves in the water, giving it alkaline properties, turning litmus blue and phenolphthalein red (Fig. 19).

Sodium Peroxid (Na_2O_2).—When sodium is heated in dry air the metal falls into a yellow hygroscopic powder. This is an oxid having the composition Na_2O_2. It is valuable as a means of preparing hydrogen dioxid for bleaching textile fabrics. Water containing it is alkaline and behaves as if it were a solution of hydrogen dioxid, in accordance with this equation:

$$Na_2O_2 + 2H_2O = 2NaOH + H_2O_2.$$

Sodium Hydroxid (NaOH) (*Sodium Hydrate, Caustic Soda*).—It has been stated above that when water acts on metallic sodium the hydroxid is produced. From the carbonate it is obtained by the action of lime-water, the calcium being precipitated as carbonate, the sodium hydroxid being left in solution:

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH.$$

It is now largely manufactured by electrolysis of sodium chlorid with mercury as a cathode to take up the metal. The amalgam in contact with water forms sodium hydroxid.

Properties.—The *hydroxid* occurs in gray-white masses or in molded sticks, closely resembling potassium hydroxid. Like that it is strongly alkaline in reaction, soapy in taste, fuses by heat, dissolves freely in water with evolution of heat, is deliquescent, and in the moist state absorbs carbon dioxid from the air, forming the carbonate. This carbonate is not deliquescent, like potassium carbonate, but efflorescent. When a can of caustic soda is opened, the solid first liquefies, then absorbs carbon dioxid, and finally solidifies in a whitish powder.

Under the name of "concentrated lye," an impure mixture of the hydroxid and the carbonate is largely used as a rapid cleanser in the laundry and in the making of soap. A child, in playing about the laundry, out of curiosity eats some of the contents of a can containing "lye." The poison, if it does not reach the stomach, corrodes the throat and leaves a stricture of the gullet, which permits swallowing of liquid food only.

Symptoms.—The symptoms are those of a corrosive poison, differing in degree only from those caused by potassium hydroxid.

Fatal Dose.—About the same as for the potassium compounds.

Fatal Period.—The duration of life will depend on the dose and the lesions, and may be described as about the same as that given for the potassium compounds.

Treatment.—The antidotes are water containing vinegar and

lemon juice to neutralize the alkali, and milk, oil, or butter to saponify it.

Post-mortem Appearances.—The toxic effect is purely local. Although less active than the potassium compounds, the caustic forms of soda dissolve the albumin of the tissue, abstract the moisture, saponify the fatty material, and corrode deeply and widely.

Detection.—The history of the case, inspection of inflamed spots on the face and hands, the strong soapy taste, and marked alkaline reaction of vomited matters will go far to prove a caustic alkali. The tests for sodium salts (see p. 229) can be applied to determine the character, making allowance for the sodium chlorid always present in food and tissue. As commercial sodium hydroxid nearly always contains a small quantity of arsenic, a trace of the latter would strengthen the evidence in favor of the caustic alkali.

Sodium chlorid, NaCl, *common* or *table salt*, is a type of neutral salts in general. Present everywhere in nature, it is essential to the process of nutrition in living things. While potassium is found in the blood-corpuscles, sodium salts are constituents of the plasma and other animal fluids. *Rock salt* is a mineral deposited at the bottom of salt lakes in former geologic eras. As obtained from the salt mines, it is colored by a trace of iron or other impurity.

Properties.—From salt waters it separates as cubic crystals enclosing a drop of the salt solution. When heated the drop passes into vapor, bursting the crystal with a crackling noise. It is freely soluble alike in cold or hot water, insoluble in absolute alcohol.

Normal salt solution is a solution of sodium chlorid (0.7 to 0.9 per cent.). It is made by dissolving 45 or 50 gr. of common salt in 1 pt. of water previously sterilized by boiling. This is injected warm beneath the skin of the buttocks in cases of loss of blood or blood-poisoning; it has about the same osmotic pressure as the blood.

On account of its cheapness sodium chlorid is the starting-point for obtaining sodium and its compounds, as potassium chlorid is, directly or indirectly, for that metal.

Sodium bromid, NaBr, can be formed by saturating a solution of the hydroxid with bromin and fusion with charcoal.

Sodium iodid, NaI, is prepared by a reaction like that used for potassium iodid. Essentially stated, ferrous iodid is acted upon by sodium hydroxid, leaving potassium iodid in solution and precipitating ferrous hydrate.

The bromid and iodid resemble the chlorid in crystallizing in

anhydrous cubes, but they are more soluble in water than is the chlorid. They are also soluble in alcohol. Dose: 5 to 60 gr. (0.3–3.5 gm.).

Sodium Nitrate ($NaNO_3$).—This corresponds to potassium nitrate, hence is called *Chili niter*, or *saltpeter*. It is found in a rainless district of Chili as solid deposits of colorless deliquescent crystals. It has a cool, bitter, saline taste with neutral reaction and is very soluble in water, but not in cold alcohol. It is the most important manure for cultivated plants. In dilute solution in the soil it is a valuable source of nitrogen for their nutrition. Dose: 8 to 40 gr. (0.5–2.5 gm.).

Sodium Sulphate (Na_2SO_4, $10H_2O$) (*Glauber's Salt*).—This occurs dissolved in many saline aperient waters. In the manufacture of nitric acid it is left in the retort:

$$2NaNO_3 + H_2SO_4 = 2HNO_3 + Na_2SO_4.$$

Indeed, it is a product of the reaction that takes place on heating sulphuric acid with sodium salts of volatile acids generally; thus in making hydrochloric acid from common salt:

$$2NaCl + H_2SO_4 = 2HCl + Na_2SO_4.$$

Properties.—It forms large, colorless prisms which effloresce in air, have a cool saline taste, and are neutral in reaction, very soluble in water, and insoluble in alcohol. It is an active purgative in the dose of 1 to 8 dr. (4–32 gm.). A teaspoonful in a large glass of water makes the intestinal contents thin and watery. The salt is not absorbed, so the osmotic pressure is high toward the intestines until their contents are of equal concentration with the body fluids.

The solution of sodium sulphate stands for but two ions: sodion Na^+ and sulphanion $(SO_4)^=$, which are present in great abundance. That the chemical activities are not due to sodium and anhydrous sulphuric acid is shown by the following facts: We have learned that it is difficult to keep the metal from passing into the condition of sodion. Notwithstanding this tendency, when sodium is absolutely dry it can be immersed in perfectly anhydrous sulphuric acid without any chemical change. This inertness disappears instantly on adding the least amount of water. The metal changes to the ion in the hydroxid $Na^+(OH)^-$. The water also gives hydrion H^+ to the sulphuric acid. Dissociation produces sodion Na^+ and sulphanion $(SO_4)^=$, the hydrion H^+ and hydroxidion $(HO)^-$ uniting and forming water which does not dissociate.

$$2Na^+, (OH)^- + H^+, H^+, (SO_4)^= = Na^+, Na^+, (SO_4)^= + 2H_2O.$$

Sodium bisulphate ($HNaSO_4$) (*sodium acid sulphate*) occurs in long four-sided crystals which decompose spontaneously into H_2SO_4 and Na_2SO_4.

Sodium Phosphates.—The theoretic relations of the three phosphates have been discussed under the head of Phosphoric Acid (p. 188). It remains to consider them practically.

Sodium Normal Phosphate (Na_3PO_4, $12H_2O$) (*Trisodium Phosphate, Basic Phosphate*).—When sodium hydroxid is added to disodium phosphate, another atom of sodium is taken, forming a salt which crystallizes in six-sided prisms. It is freely soluble in water, with an alkaline reaction, absorbing water and carbon dioxid from the air to form Na_2CO_3 and reverting to the more stable salt, HNa_2PO_4.

Sodium Neutral Phosphate (HNa_2PO_4, $12H_2O$) (*Sodium Orthophosphate, Disodium Phosphate*).—This is prepared by the reaction between monocalcium phosphate and sodium carbonate:

$$Ca(PO_4H_2)_2 + 2Na_2CO_3 = CaCO_3 + 2HNa_2PO_4 + H_2O + CO_2.$$

It crystallizes in beautiful rhombic prisms which effloresce, losing $5H_2O$, hence it should be kept in well-stoppered bottles. It is very soluble in water, with a feeble alkaline reaction to litmus, but not to phenolphthalein (see p. 130). When a solution of the salt is saturated with carbon dioxid the liquid colors blue litmus red and red litmus blue, and it is said to have an *amphoteric reaction*. Human milk and urine show this reaction not infrequently. It is present in the blood and other animal fluids. Under the name *sodii phosphas* (U. S. P.) it is used in medicine as a laxative and biliary stimulant. Dose: 1 to 8 dr. (4–32 gm.). Its incompatibles are lead acetate, carbolic acid, chloral hydrate, antipyrin, alkaloids, salicylic acid, and sodium salicylate.

Liquor sodii phosphatis compositus is a concentrated solution of HNa_2PO_4 with sodium nitrate and citric acid. Each cubic centimeter contains 1 gm. of the phosphate. Dose: $\frac{1}{2}$ to 2 f. dr. (2–8 c.c.).

Sodium acid phosphate (H_2NaPO_4) (*monosodium phosphate*) is formed by treating disodium phosphate with phosphoric acid:

$$Na_2HPO_4 + H_3PO_4 = 2NaH_2PO_4.$$

It crystallizes in two forms and dissolves in water, forming an acid solution. It is present in the urine, imparting to that fluid an acid reaction (see p. 599).

Sodium Carbonate (Na_2CO_3, $10H_2O$) (*Normal Carbonate, Disodium Carbonate*).—Under the name of *sal soda* or *washing soda* this is used as a domestic article to soften water and assist

in cleansing. It occurs in rhombic octahedrons or in large angular masses which effloresce and crumble to powder. It is alkaline, acrid in taste, soluble and caustic, in every respect like the corresponding salt of potassium only less severe.

Of the several methods of manufacture the *Solvay ammonia process* is the most economic. The reaction is between sodium chlorid and ammonium bicarbonate, the products being ammonium chlorid, which remains dissolved, and sodium bicarbonate, which is only sparingly soluble and therefore separates:

$$NH_4HCO_3 + NaCl = NH_4Cl + HNaCO_3.$$

The bicarbonate, $HNaCO_3$, when collected, dried, and heated, yields the carbonate, water, and carbon dioxid:

$$2HNaCO_3 = Na_2CO_3 + H_2O + CO_2.$$

The *cryolite process* is to heat that mineral, a double sodium and aluminium fluorid, with limestone:

$$\underset{\text{Cryolite.}}{Al_2Na_6F_{12}} + \underset{\text{Limestone.}}{6CaCO_3} = \underset{\text{Calcium fluorid.}}{6CaF_2} + \underset{\text{Sodium aluminate.}}{Na_6Al_2O_6} + 6CO_2.$$

The sodium aluminate is dissolved out with water and treated with the CO_2 given off in the first stage:

$$\underset{\text{Sodium aluminate.}}{Na_6Al_2O_6} + 3H_2O + 3CO_2 = \underset{\text{Sodium carbonate.}}{3Na_2CO_3} + \underset{\text{Aluminium hydrate.}}{2Al(OH)_3}$$

When the crystals of carbonate effloresce and are then dried at 45° C. to half their weight they form the white powder, *sodii carbonas monohydratus* (U. S. P.), $Na_2CO_3H_2O$.

Sodium carbonate is a caustic alkali and, hence, is not given internally, unless in small doses of 5 to 10 gr. (0.32–0.65 gm.) largely diluted. The antidotes for it are the diluted acids, vinegar, lemon juice, and the oils with milk.

Sodium bicarbonate ($NaHCO_3$) (*acid carbonate, monosodium carbonate*) occurs in Vichy and many other alkaline mineral waters. It can be made by the Solvay ammonia process given above, or by the action of carbon dioxid on the normal carbonate. Its crystals are without water and are permanent in the air. It is soluble in water, imparting a saline taste and an alkaline reaction. As carbonic acid is a very weak acid and its salts are hydrolyzed in solution, all soluble carbonates dissociate enough hydroxyl to give an alkaline reaction, the carbonic acid remaining almost undissociated:

$$Na_2CO_3 + H_2O = Na^+, (HCO_3)^- + Na^+, (OH)^-.$$

$$NaHCO_3 + H_2O = Na^+, (OH)^- + H_2CO_3.$$

If the monosodium carbonate is put in water and boiled, it loses CO_2 and dissolves as the disodium carbonate. If this is evaporated rapidly a salt separates, called the *sesquicarbonate*, $Na_4H_2(CO_3)_3$, sometimes written Na_2CO_3, $NaHCO_3$, $2H_2O$.

Sodium bicarbonate is commonly called *bread soda* or *cooking soda*, to distinguish it from the other domestic salt, *washing soda*, from which it differs in the mildness of its local effects, being without caustic action. It is given internally in doses of 10 to 40 gr. (0.6–3 gm.) as an antacid.

As it is harmless internally and is a convenient source of carbon dioxid gas, it is extensively used as a substitute for yeast in "baking powders" to "aerate" or "raise" bread. One kind of baking powder widely used is made by mixing a pound of potassium bitartrate with half a pound of sodium bicarbonate. A sufficient quantity is mixed with the dough, and in the process of baking the acid in the tartrate is neutralized by the sodium, and the gas CO_2, liberated in bubbles, disseminated through the bread, making it light and permeable by the digestive fluids. The equation is:

$$\underset{\text{Sodium bicarbonate.}}{NaHCO_3} + \underset{\text{Cream of tartar.}}{HKC_4H_4O_6} = \underset{\text{Sodium-potassium tartrate.}}{NaKC_4H_4O_6} + H_2O + CO_2.$$

Another kind of baking powder which is considered hurtful because of the aluminium it contains is made by mixing common alum, or aluminium sulphate, with the sodium bicarbonate:

$$\underset{\text{Sodium bicarbonate.}}{6NaHCO_3} + \underset{\text{Aluminium sulphate.}}{Al_2(SO_4)_3} = \underset{\text{Sodium sulphate.}}{3Na_2SO_4} + \underset{\text{Aluminium hydrate.}}{2Al(HO)_3} + 6CO_2.$$

Sodium-potassium tartrate ($NaKC_4H_4O_6$, $4H_2O$) (*potassii et sodii tartras*, U. S. P.), *Rochelle salt* may be obtained in colorless crystals, though usually it is a white powder, of a bitter, saline taste, neutral in reaction, freely soluble in water. It is a mild laxative in doses of 4 to 8 dr. (8–32 gm.).

Pulvis Effervescens Compositus (U. S. P.) (*Seidlitz Powder*).—This is a preparation for administering Rochelle salt in an effervescing draught to conceal the bitter taste. One powder is in two papers, the blue and the white. The blue paper contains Rochelle salt, 2 dr., and sodium bicarbonate, 40 gr.; the white paper contains tartaric acid, 35 gr. If dissolved separately and the two solutions mixed there is brisk effervescence, due to the escape of the CO_2. One or two of them may be taken while effervescing.

Tests for Sodium.—(1) The most sensitive and readiest means of recognizing sodium is the bright-yellow color it imparts to the colorless flame of a Bunsen burner. The spectroscope places the sodium flame as an intense line in the pure yellow, cor-

responding to *D* in the solar spectrum. As all bright flames under ordinary circumstances show this *D* line, it is inferred that a trace of sodium is almost universal. Continued heat soon volatilizes this accidental trace of sodium on platinum wire. When the amount is appreciable by weight, say as much as 1 mg., the bright-yellow color lasts so much longer that the experienced analyst easily distinguishes it from the accidental trace (Fig. 19).

(2) The salts of sodium are all white and are non-volatile to red heat. As they are all soluble in water, no ordinary reagent precipitates them. With the anions of hydrofluosilicic acid $(SIF_6)^=$, and pyroantimonic acid $(Sb_2O_7)^=$, it forms compounds of low solubility.

LITHIUM

Symbol, Li. Atomic weight, 7.

This metal occurs in combination in mineral waters and as a silicate in *lepidolite*.

Properties.—Lithium resembles sodium in many respects, being silver white and ductile. With a specific gravity of 0.59 it is the lightest metal. It floats upon water, decomposing it, but not igniting the hydrogen. It burns at 200° C. (392° F.) with a crimson flame. Its compounds do not differ much from those of sodium. Its hydroxid reacts strongly alkaline. The salts used in medicine are the bromid, citrate, and carbonate.

Lithium bromid, LiBr, is obtained by saturating with lithium carbonate a solution of hydrobromic acid. It forms crystalline needles that are very deliquescent and soluble in water and alcohol. Dose: 5 to 20 gr. (0.32–1.3 gm.). Its incompatibles are the acids; the salt of antimony, bismuth, silver, lead, mercury, copper; and the alkaloids.

Lithium carbonate, Li_2CO_3, is a white alkaline powder, only sparingly soluble in water, but more soluble in carbonated water, which converts it into the bicarbonate. Dose: 5 to 15 gr. (0.32–1 gm.).

Lithium citrate, made by the action of citric acid on the carbonate, is much more soluble than the carbonate. Dose: 5 to 15 gr. (0.32–1 gm.).

Lithii citras effervescens is a granular solid, containing 5.0 per cent. of the citrate mixed with enough sodium bicarbonate with tartaric and citric acids to react when dissolved, liberating carbon dioxid and forming neutral salts.

Lithium urate is the compound made by the metal with uric acid of the body. It is more soluble than the natural urates, and hence lithium salts are given to dissolve urate deposits in the joints.

Tests for Lithium.—(1) Lithium is identified by the red color of its flame. The spectroscope shows two bright lines, one red and the other yellow, distinct from the sodium line (Fig. 19).

(2) Concentrated solutions are precipitated by ammonium carbonate as white lithium carbonate.

RUBIDIUM

Symbol, Rb. Atomic weight, 85.4.

Although widely distributed in nature, the quantity of rubidium obtainable by convenient processes is very small. It gets its name from the two dark-red lines of its spectrum (Fig. 19). The metal and its compounds resemble potassium and its compounds very closely—physically, chemically, and medically. Its presence is doubtful if it cannot be identified by the color of its flame. It is separated from potassium by the fact that the double salt with platinum chlorid is a little less soluble than the corresponding potassium salt.

CESIUM

Symbol, Cs. Atomic weight, 132.81.

This is an extremely rare metal, discovered by the two sky-blue lines of its spectrum (Fig. 19). It resembles rubidium and potassium, with more chemical energy than either, being the strongest base-former of all the elements.

AMMONIUM

Formula, NH_4. Molecular weight, 18.

A class of compounds closely resembling, physically and chemically, those of potassium has been found to contain the group NH_4. When solutions of these salts are electrolyzed, the cation is $(NH_4)^+$, and if mercury be used as a cathode, an amalgam is formed like that of potassium. Although the group has never been isolated as a metal, the ion is so much like the univalent cations of alkali salts that it is considered to belong to the same family with the alkali metals.

Ammonia (NH_3) (*Volatile Alkali*).—This occurs in nature in small amounts widely distributed. A trace is present in the air and in surface waters that have been contaminated by nitrogenous waste. It is evolved from stable manure, and in the soil is most important as a source of nitrogen for the growth of plants.

Preparation.—Ammonia is formed by direct union of hydrogen and nitrogen under high temperature and pressure, by putrefaction or destructive distillation of protein substances, and by heating ammonium hydroxid: $NH_4HO = NH_3 + H_2O$. The most

convenient method is to heat an ammonium salt with a strong base, such as an alkaline hydroxid or lime:

$$\underset{\text{Ammonium chlorid.}}{2NH_4Cl} + \underset{\text{Calcium hydroxid.}}{Ca(OH)_2} = \underset{\text{Calcium chlorid.}}{CaCl_2} + 2H_2O + \underset{\text{Ammonia.}}{2NH_3}$$

Properties.—Ammonia, NH_3, is a colorless gas having a pungent odor, irritating to the eyes and the mucous lining of the air-passages, and turning moist red litmus-paper blue. Under a pressure of $6\frac{1}{2}$ atmospheres at 10° C. (50° F.) it is condensed to the liquid used in ice-machines to create a freezing temperature by its evaporation. *Ammonium hydroxid* is a strong solution of the gas in water. Water will absorb 700 times its volume at ordinary temperatures and thereby acquire the alkalinity, the pungency, and the chemical properties of the gas itself (Fig. 60). This is regarded as an act of chemical union in which the *anhydrid* NH_3, unites with H_2O to form the hydroxid NH_4OH.

The liquefied ammonia gas, NH_3, is used in ice-factories and refrigerators. Occasionally the receivers burst and the vapors fill the room, with deadly consequences to those who are exposed to them. To arouse fainting persons it is sometimes given too strong by inhalation.

Ammonium Hydroxid (NH_4OH) (*Ammonia Water*).—When ammonia is dissolved in water a compound is formed which neutralizes acids and forms salts; hence, it is basic. As the basicity is due to hydroxidion the dissociation of ammonium hydroxid is represented by the equation—

$$NH_4OH = (NH_4)^+, (OH)^-.$$

The smell of the solution shows that some portion of the ammonia is still in the condition of the uncombined gas. The amount of hydroxyl dissociated is not so great as with potassium hydroxid or sodium hydroxid, as is shown by the lower electric conductivity. In spite of the irritant action on the mucous membranes and the strong impression made on the olfactory nerves, ammonium hydroxid is not a strong base. Still, it readily forms salts with all acids.

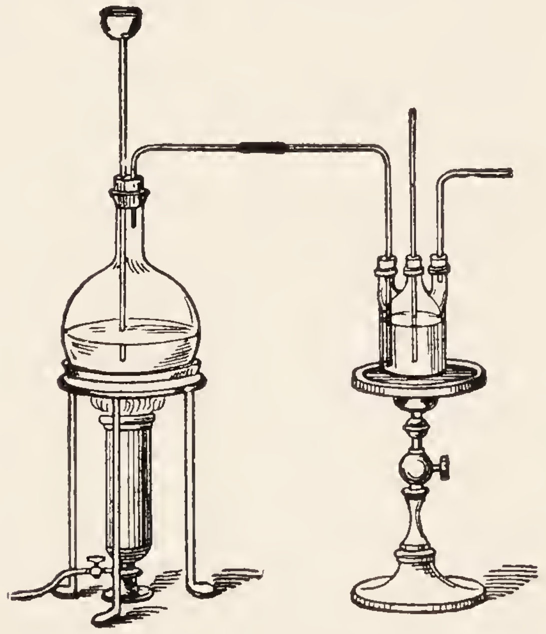


FIG. 60.—Charging water with soluble gas.

Under the names of *hartshorn* and *ammonia*, ammonium hydroxid is largely used in the household as a cleansing agent to remove paint, oil, and dirt generally from clothing; hence it is easy to have accidental poisoning with it.

Pharmaceutic Preparations.—*Aqua ammoniæ fortior* (U. S. P.) contains 28 per cent. by weight of ammonia gas, has a specific gravity of 0.897, and is a powerful corrosive. It is incompatible with acids, alkaloids, chlorin water, iodin, bromin, and most metallic salts. *Aqua ammoniæ* (U. S. P.) has 1½ times more water, only 10 per cent. of ammonia gas, and a specific gravity of 0.958. Dose: 10 to 30 ♏ (0.60–1.90 c.c.). *Spiritus ammoniæ* (U. S. P.) is a solution of the gas in alcohol, of the same strength as the aqua, and better adapted for internal use. When it has added to it the carbonate, with small quantities of oils of nutmeg, lemon, and lavender, the *aromatic spirits* is produced. Dose: 1 to 2 fl. dr. (3.75–7.50 c.c.). *Ammonii carbonas* occurs as whitish angular masses, giving off the characteristic irritating and alkaline vapor of ammonia, and caustic in strong solution (p. 235).

Symptoms.—The nature and gravity of the effects will depend greatly on concentration of the solution, and on whether or not the subject received a large dose of the vapor by the lungs. The direct chemical action upon vital tissue is the same as that of potassium hydroxid, though less in degree—that is, the albumin is dissolved, the fatty matter saponified, and the water abstracted. The respiratory symptoms are a suffocative feeling due to spasm of the glottis, followed by a sense of pain and weight in the chest, with an irritative cough due to inflammation of the larynx and trachea.

The symptom due to the local caustic effect of the fluid is burning pain in the mouth and throat, extending to the stomach if the poison went so far. There are salivation, vomiting, and difficulty in swallowing. As a result of a free absorption of the poison by the lungs and stomach, cases display grave remote effects sometimes with great rapidity. The heart's action is sometimes arrested in a few minutes; sometimes there is immediate unconsciousness with coma, and death in a few minutes; sometimes there is unconscious delirium, soon ending in death.

Fatal Dose.—A teaspoonful of the stronger aqua ammoniæ has in at least one instance proved fatal, and two fluidrams have caused death in two or three other cases. Recovery, however, has sometimes followed much larger doses, such as a tablespoonful, and even upward of a fluidounce has been taken without fatal results.

Fatal Period.—By suffocation and syncope death has occurred in four minutes after inhalation of the gas. On the other hand, death may occur after many months as a result of the starvation due to stricture of the gullet or pylorus.

Treatment.—The antidotes are weak vinegar, lemon juice, oil, butter, and milk. The sequels are to be treated as they arise.

Postmortem Appearances.—These are not markedly different from the inflamed state of the alimentary tract as caused by the other caustic alkalis. When the vapor acts as an irritant upon the air-passages, an inflamed state of the larynx and even of the bronchi may be found.

Ammonium chlorid (NH_4Cl) (*sal ammoniac*) is produced from the ammonia liquor of gas works by neutralizing with hydrochloric acid and evaporating. Although it forms a white crystal of the regular system it is usually found in tough fibrous masses, salty in taste, without odor and freely soluble. At 450° C. (862° F.) it passes into colorless vapors, which, if water be present, are a mixture of NH_3 and HCl. Although a neutral salt, the aqueous solution is feebly acid, owing to the slight hydrolysis to be expected with a salt of a weak base. Some ammonion unites with the hydroxidion of the water to form NH_4OH:

$$NH_4Cl \quad + \quad H_2O \quad = \quad NH_4OH \quad + \quad H^+, Cl^-.$$

The weak ammonium hydroxid is dissociated to a much lower degree than is the strong acid hydrochloric. The excess of hydrion causes the acid reaction. If the solution be boiled, a portion of ammonia escapes and the acid reaction increases.

The facility with which it splits off hydrogen chlorid makes it useful as a flux to clean metallic surfaces for soldering and as an exciting salt in the Leclanché battery cell. Dose: 5 to 20 gr. (0.32–1.29 gm.) (p. 47).

Ammonium nitrate, NH_4NO_3, can be obtained by neutralizing nitric acid with ammonium hydroxid. The solution evaporated yields long flexible prisms. Heated to 150° C. (302° F.), the dry salt fuses, and at 210° C. (410° F.) decomposes into nitrous oxid and water:

$$NH_4NO_3 \quad = \quad N_2O \quad + \quad 2H_2O.$$

When quickly heated to a high temperature, it yields a large volume of mixed gases—ammonia, nitric, and nitrous oxids; hence, is used as an explosive.

Ammonium acetate, $NH_4C_2H_3O_2$, is official in aqueous solution as *liquor ammonii acetatis* (U. S. P.) (*spirit of mindererus*), an antipyretic in doses of 2 to 8 f. dr. (7.4–30 c.c.). This is a 7 per cent. solution of a salt made by saturating dilute acetic acid with ammonium carbonate.

Ammonium carbonate [$(NH_4)_2CO_3,H_2O$] (*normal carbonate, diammonium carbonate*) is formed as a white crystalline solid and is not stable. In air it breaks down rapidly into ammonia and a white powder of the acid carbonate:

$$(NH_4)_2CO_3 \quad = \quad NH_3 \quad + \quad NH_4HCO_3.$$

Ammonium bicarbonate (NH_4HCO_3) (*acid carbonate, monoammonium carbonate*) is prepared by saturating ammonia water with carbon dioxid. It crystallizes in large rhombic prisms, stable, and freely soluble in water. Heated to 60° C. (140° F.) it breaks up into $NH_3 + H_2O + CO_2$.

Ammonium sesquicarbonate (*ammonii carbonas*, U. S. P., *sal volatile*, *Preston salts*) is a combination of the acid carbonate described above: NH_4HCO_3 with a variable amount of salt of carbamic acid, called *ammonium carbamate*, $NH_4CO_2NH_2$, which appears to be the carbonate deprived of water:

$$(NH_4)_2CO_3 \quad - \quad H_2O \quad = \quad NH_4CO_2NH_2.$$

The combined salts crystallize in hard translucent rhombic prisms with a pungent odor and an alkaline reaction. When this changes to the acid carbonate it may be used, in whole or in part, in place of sodium bicarbonate in baking powders. When used alone to aërate pastry, by the heat of the oven, it is all converted to H_2O and the gases NH_3 and CO_2. Dose: 5 to 20 gr. (0.32–1.29 gm.). Its incompatibles are the acids, acid salts, alum, alkaloids, and most metallic salts.

Ammonium Sulphid $(NH_4)_2S$.—By saturating strong ammonium hydroxid with hydrogen sulphid in excess there is formed in solution ammonium hydrosulphid, NH_4HS. To obtain ammonium sulphid, an equal volume of ammonium hydroxid must be added, so as to replace the second hydrogen atom. The solution containing $(NH_4)_2S$ is at first colorless, with a disagreeable odor, but soon turns yellow in the air from oxidation and separation of sulphur, part of which dissolves, forming polysulphids, and part is precipitated. It is used as a reagent to precipitate the heavy metals, the sulphids of which are soluble in free acids. It is also employed in organic chemistry as a reducing agent. The yellow sulphid is used to dissolve the sulphids of arsenic, antimony, and tin in analytic operations.

Ammonium Phosphates.—There are three possible phosphates, but the normal salt is too unstable to keep. The mono and diammonium phosphates exist, but are insignificant.

Ammonium-sodium phosphate, ($HNaNH_4PO_4$, $4H_2O$), is called *microcosmic salt* because it is in the residue of evaporated stale urine of man, the microcosm. It is much used in blowpipe work to make a colorless bead on the platinum loop. Metallic compounds color the bead in characteristic tints.

Tests for Ammonium Salts.—Ammonia gas turns red litmus-paper blue, and makes a white smoke when mixed with the fumes of a rod wet with hydrochloric acid. All salts are volatile when heated, and evolve the gas spontaneously or when heated with

calcium hydroxid. Platinum chlorid yields a yellow precipitate like that given by potassium. Not only does ammonium form salts, like those of potassium, of feeble solubility with the anion of chlorplatinic acid, but also with the anion of tartaric acid and the cobaltinitrite ion (p. 222).

Detection of Ammonium Salts.—Owing to the volatility of ammonia, its hydroxid and its carbonate, these soon escape from the body. During life or soon after death detection is easy by the characteristic odor. If the volatile preparation has been fixed by the antidote, the vapor can be developed by heating the material with lime. This vapor will be alkaline and form white fumes with hydrochloric acid.

If the organic material to be examined is putrid, allowance must be made for the ammonia produced by putrefaction. This is never enough to develop the dense white fumes of ammonium chlorid from a rod wet with hydrochloric acid. The amount may be estimated by distillation, neutralizing the distillate with hydrochloric acid, evaporating nearly to dryness, and precipitating the double chlorid of ammonium and platinum by adding excess of alcoholic solution of platinum chlorid. After filtration the precipitate is washed with alcohol, dried, and weighed; 100 parts represent 8.6 parts of ammonia, NH_3.

The Energy of Alkali Metals.—The chemical energy of all the members of this group is partly expressed in the statement that their ions are electropositive and univalent. Univalent metals carry but one electric charge, and, according to Faraday's law, the amounts of electricity set in motion are the same for each atom of an alkali metal. In the passage of free alkali metals to the ion state they take up equal *quantities* of electricity, as their *capacities* are equal. Their differences of energy find an explanation in the other factor, the *potential* or intensity with which they work. The ions of potassium with a higher potential are discharged under certain conditions with greater readiness or velocity than those of sodium and ammonium.

II.—METALS OF THE ALKALINE EARTHS

The alkaline earths—lime, CaO, baryta, BaO, strontia, SrO, and magnesia, MgO, are oxids with a reaction like the caustic alkalis, though they are much less soluble. The metals form divalent ions exclusively, are heavier than water, decompose water slowly, form normal carbonates and phosphates insoluble in water, but soluble when carbon dioxid is in solution, and form hydroxids that are sparingly soluble.

CALCIUM

Symbol, Ca. Atomic weight, 40.09.

Occurrence.—In the form of silicates and carbonates this metal is very abundant and widely distributed in nature. *Marble* is the carbonate crystallized; *limestone* and *chalk*, the same salt less pure. It is also present in the shells of eggs and molluscs. *Gypsum* is the sulphate. The bones of animals are rich in the phosphate.

Preparation.—Calcium is separated from the iodid by metallic sodium:

$$CaI_2 + 2Na = 2NaI + Ca.$$

When pure it is grayish-white, like polished iron, and fairly hard. Water attacks it slowly, and it unites with oxygen when heated.

Calcium oxid (CaO) (*Calx*, *Quicklime*).—This is obtained by heating the carbonate, as *limestone* or *marble*, in limekilns:

$$CaCO_3 \rightleftarrows CO_2 + CaO.$$

Carbonic acid is so weak that it cannot only be expelled by other acids, but even driven away as anhydrid by strong heat.

Lime is a white, amorphous, almost infusible, powder. Exposed to the air it becomes *air-slaked*—that is, it absorbs moisture, forming hydroxid:

$$CaO + H_2O = Ca(OH)_2.$$

At the same time the calcium hydroxid takes carbon dioxid to form calcium carbonate, so that it soon becomes chemically inert.

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

The absorption of CO_2 from the air to form $CaCO_3$ is practically a reversal of the reaction by which the CO_2 was driven off in lime burning. If that operation is carried on in a closed flask the pressure and the temperature determine the result just as they determine whether water shall remain liquid or boil off in vapor. At ordinary temperature in the open there is more pressure of CO_2 in the atmosphere than the decomposition pressure of $CaCO_3$; hence the reaction is reversed and CO_2 is absorbed.

The question of the degree of dampness in a room may be settled by closing it hermetically, weighing a dish, and putting on it 1 kg. (2 lb.) of *quicklime*, and exposing it for twenty-four hours. If the kilogram gain in weight 1 gm., or the 2 lb. Troy gain 12 gr., then the room is too damp to be wholesome.

When lumps of quicklime are mixed with water, the water is absorbed, heat is evolved, the lime swells and breaks down into a white powder, which if added to more water remains for a time mechanically suspended as *whitewash* or *milk of lime*. Eventually this settles and a very small percentage (0.14 per cent. or 1.4 gm. per L.—less than 1 gr. to 1 f. oz.) is left dissolved to make *lime-water* or *liquor calcis* (U. S. P.). Its electric conductivity shows that dissociation is almost complete. The following equation exhibits a relatively large amount of hydroxidion:

$$Ca(OH)_2 \quad = \quad Ca^{++}, (OH)^-, (OH)^-.$$

These hydroxyl ions give it an alkaline reaction to litmus and confer upon it strong basic properties. Owing to its feeble solubility there is very little concentration of these ions; hence, *lime-water* is used in the laboratory and medicine when very limited basic or antacid effects are desired. It is a clear, colorless, odorless liquid of feeble taste and sedative action. The *milk of lime* or *lime paste* is quite irritating to the stomach, acting like the caustic alkalis and sometimes causing dangerous inflammation. The antidotes are dilute vinegar, lemon juice, and the oils. Lime-water is kept standing over the excess of lime, so that it renews its strength as fast as the surface layers take up carbon dioxid from the air to be precipitated as calcium carbonate. When the gas is passed through lime-water, this salt separates and imparts a milky appearance. *Mortar* and *plaster* are mixtures of sand, slaked lime, and water, which slowly change by exposure to air to a hard mass of calcium carbonate and calcium silicate. In doing so they liberate water, making the wall damp for months together, unless the process be hastened by open coal fires.

Fresh milk of lime is used in chamber vessels to disinfect urine, vomit, and feces. As *whitewash*, it disinfects the walls of cellars.

Syrupus Calcis (U. S. P.) (*Syrup of Lime, Saccharated Solution of Lime*).—The solubility of lime is much increased by adding sugar. The amount dissolved is 7 or 8 gr. to 1 fl. oz. when 5 per cent. of lime and 30 of sugar are boiled in 100 of water. The dose, as an antidote to oxalic and carbolic acids, is from $\frac{1}{2}$ to 2 dr. (1.95–7.80 gm.). Lime-water and the syrup are incompatible with acids and metallic salts generally.

Linimentum calcis (U. S. P.) (*carron oil*) contains equal parts of lime-water and linseed oil. It is a calcium soap.

Soda lime is a mixture of quicklime and sodium hydroxid, dried. It is used in the laboratory for absorbing carbon dioxid from mixed gases.

Calcium chlorid is used as a desiccating agent in the laboratory, in the form of a dried spongy mass. It is less perfect in

this respect than sulphuric acid. In the anhydrous condition it is a colorless salt of great solubility. With water it forms five different hydrates. The hexahydrate, $CaCl_2, 6H_2O$, occurs in large deliquescent crystals, which on heating lose water, becoming anhydrous. Dose as an antistrumous alterative: 5 to 20 gr. (0.32–1.2 gm.).

Calcium Hypochlorite ($CaOCl_2$) (*Calx Chlorinata*, U. S. P., *Bleaching Powder*).—This substance has been fully considered under the head of hypochlorous acid (see p. 140). It does not contain calcium chlorid in the form of a mechanical mixture, as it does not deliquesce. When dissolved in water it dissociates in the same way as it would if there were calcium chlorid in it, though its composition is best expressed by the formula $Ca{<}^{Cl}_{OCl}$:

$$2Ca{<}^{Cl}_{OCl} = Ca^{++}, Cl_2^{-} + Ca^{++}, (OCl)^{-}(OCl)^{-}.$$

Calx Sulphurata (U. S. P.) *Sulphurated Lime*.—By heating together a mixture of calcium sulphate, starch, and charcoal, a compound is obtained which is misnamed *calcium sulphid*. It contains the sulphid CaS and also the sulphate $CaSO_4$ in varying proportions, not less than 55 per cent. of CaS. It is a grayish-white offensive powder with an alkaline reaction, slightly soluble in water, and used internally to combat suppuration. Dose: $\frac{1}{10}$ to $\frac{1}{2}$ gr. (0.006–0.032 gm.).

Calcium Carbid (CaC_2).—When carbon and lime are heated to the high temperature of an electric furnace they unite, carbon monoxid being set free:

$$3C + CaO = CaC_2 + CO.$$

While calcium carbid can be obtained pure as transparent crystals, the commercial product comes in grayish-brown hard lumps, with the odor of garlic or phosphureted hydrogen. Its value is due to the fact that it is decomposed by water with the formation of acetylene gas and calcium hydroxid :

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2.$$

The gas burns in air with a sooty flame which, when special burners are used to insure a larger proportion of oxygen, changes to an intensely white light. As acetylene is an explosive substance, when mixed with air or oxygen, great care should be used with the apparatus for generating it on a large scale (p. 384). The brightness of the flame is due to the enormous energy absorbed from the electric furnace in the manufacture of CaC_2

and set free in the combustion of acetylene. It is 223 kilojoules more than that produced by burning the same amount of free C and H. The greater the heat, the brighter the light.

Calcium Carbonate ($CaCO_3$).—The purest natural forms of this salt are *Iceland spar*, *calc spar*, or *calcite*, in rhombohedra; and *arragonite*, in rhombic prisms. Less pure, but still crystalline forms, are *marble* and *limestone*. *Chalk* is composed of minute grains of calcium carbonate.

Creta Præparata (U. S. P.) (*Prepared Chalk*).—The native chalk is freed from coarse mineral impurities by grinding it finely and suspending the finer particles in water, the coarser ones settling first. Prepared chalk is a white amorphous powder, without odor or taste, and insoluble in water. It is used as an astringent and antacid. Dose: 5 to 30 gr. (0.32–1.94 gm.).

Mistura cretæ (*chalk mixture*) is made by rubbing together chalk, sugar, gum, and cinnamon water. Dose: 2 f. dr. (7.39 c.c.).

Calcii carbonas præcipitatus, $CaCO_3$, is made by mixing solutions of calcium chlorid and sodium carbonate:

$Ca(OH)_2$. of Ca^{++}

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$$Na^+, Na^+, (CO_3)^= + Ca^{++}, Cl^-, Cl^- = Na^+, Cl^- + Na^+, Cl^- + CaCO_3.$$

It is formed whenever calcion, Ca^{++}, meets carbanion, $(CO_3)^=$, and is a fine, impalpable white powder, odorless and tasteless, insoluble in water, but soluble in water charged with carbon dioxid.

Liquor Calcii Bicarbonatis (*Calcium Bicarbonate*).—The increased solubility of calcium carbonate in carbonic acid water is due to the formation of calcium bicarbonate, $Ca(HCO_3)_2$. This salt has not been isolated, as evaporation leaves the original carbonate, by loss of an equivalent of H_2CO_3.

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2.$$

This is a property that provides for an important movement of calcium in nature. Ground-waters charged with carbon dioxid are able to dissolve calcium carbonate from minerals and carry it to distant points to deposit it again when the gas evaporates. In this way are the stalactites of caves built up, layer on layer. In the ocean fishes and other marine animals get their calcareous skeletons from the calcium thus washed down by the rivers; in time their bones and shells make the chalk, limestone, and marble deposits.

Waters charged with minerals are unsuitable for washing purposes because of their *hardness*. They form *hard* or insoluble salts with soap. By boiling, the water loses a portion of its hardness, owing to the escape of the carbon dioxid and the precipitation

of the calcium carbonate. This lost part is said to be *temporary*, the remainder, due to other salts, is called *permanent* hardness. The crust in steam boilers is due to the solid residue of minerals left when the water has boiled off.

Calcium sulphate, $CaSO_4.2H_2O$, occurs native in great abundance as *gypsum* and *selenite*. It is also found in natural waters in small quantities, as it takes 500 parts of water to dissolve it. When heated to 107° C. (225° F.) it loses three-fourths of the $2H_2O$ it contains and is then known as *plaster-of-Paris*, *calcii sulphas exsiccatus* (U. S. P.). The expulsion of part of its water has left the crystals as a white powder which, if supplied, takes up water again and solidifies in a few minutes as crystalline gypsum. It expands as it hardens and, therefore, makes a sharp cast of statuary and masonry decorations in relief. With it dentists make molds of the gums for shaping artificial teeth, surgeons apply it as a paste to bandages, which harden to immovable dressings. The finest plaster is used by dentists. This sets too quickly for the surgeon, who generally wants more time and who, therefore, chooses the medium grade. If common salt or alum be put in the water, the bandage dries more quickly. A mixture of dry calcium sulphate and common meal is used as a rat poison; after eating it and drinking water the plaster formed solidifies in the stomach.

The **calcium phosphates** are three in number: the *tertiary* or normal, $Ca_3(PO_4)_2$; the *secondary*, $Ca_2H_2(PO_4)_2$; and the *primary* or acid, $CaH_4(PO_4)_2$, called *superphosphate*. In these formulas, owing to the divalence of calcium, the formula of phosphoric acid is doubled thus: $H_6(PO_4)_2$, which permits of substitution of Ca^{++} for two atoms of H.

Tricalcium phosphate, $Ca_3(PO_4)_2$, is the normal or bone phosphate. This is the most abundant mineral in the bodies of animals, giving solidity to the bones and supplying an essential principle to cell formation generally. In the soil it occurs in beds of phosphate rock, consisting of the skeletons of minute organisms.

Calcii phosphas præcipitatus (U. S. P.) is prepared by calcining bones, dissolving the ash in hydrochloric acid, and precipitating with ammonium hydroxid. It is a white, tasteless, odorless powder, insoluble in water and in alcohol. Dose: 5 to 30 gr. (0.32–1.94 gm.). It is inert unless dissolved by the aid of some weak acid.

Syrupus calcii lactophosphatis is a preparation of the phosphate made soluble by a little lactic and phosphoric acids, and palatable by sugar and orange-flower water. Dose: 1 to 2 f. dr. (3.70–7.39 c.c.). The solubility is due to a change of constitution: if a weak acid has been used, the secondary phosphate results; if a

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strong acid then the primary phosphate forms. Both are quite soluble in water. Thus, with a little hydrochloric acid, diluted:

$$\underset{\text{Tertiary phosphate.}}{Ca_3(PO_4)_2} + 2HCl = CaCl_2 + \underset{\text{Secondary phosphate.}}{2(CaHPO_4)}$$

By adding concentrated sulphuric acid to the bone phosphate, the primary or acid salt is formed:

$$\underset{\text{Tricalcium phosphate.}}{Ca_3(PO_4)_2} + 2H_2SO_4 = 2CaSO_4 + \underset{\text{Monocalcium phosphate.}}{CaH_4(PO_4)_2}$$

Some calcium phosphate is indispensable to the growth of plants. Removal of crops impoverishes the soils to such an extent that phosphatic fertilizers and animal manures must be used to restore their fundamental plant food. It is not easy for plants to absorb *bone meal*, though it is slowly dissolved in the soil. But the soluble acid phosphate under the name of *superphosphate*, restores to the soil in a highly assimilable form that which it had lost.

Test for Calcium.—(1) In solution a calcium salt is precipitated by a soluble carbonate, such as sodium or potassium carbonate, in the form of calcium carbonate.

(2) Potassium oxalate or ammonium oxalate makes a white precipitate of calcium oxalate insoluble in acetic acid, but soluble in hydrochloric or nitric acids.

(3) A concentrated solution of a calcium salt yields a white precipitate to sulphuric acid.

(4) From concentrated calcium solutions the hydroxids of sodium or potassium precipitate white calcium hydroxid. Ammonium hydroxid does not precipitate calcium.

(5) Its flame reaction is orange-red in color. The spectrum shows lines in the orange-red, green, and blue.

MAGNESIUM

Symbol, Mg. Atomic weight, 24.32.

Occurrence.—This metal is found in considerable quantities, widely distributed, in nature in the minerals: *magnesite*, a carbonate; *dolomite*, a mixed carbonate of calcium and magnesium; *kainite*, a double sulphate of magnesium and potassium and various silicates, such as *soapstone*, *asbestos*, *mica*, *serpentin*, *meerschaum*, and *hornblende*, capable of standing high temperatures.

Preparation.—Large amounts are now separated by electrolysis of fused *carnallite*, which contains magnesium chlorid.

Properties.—Magnesium is a white, tough metal, which remains untarnished in dry air for a long time, but in boiling

water it slowly evolves hydrogen. It dissolves readily in dilute acids, evolving hydrogen. It burns in air with an intense white flame, useful in photographing. To make a *flash-light* the powder may be blown through a flame or ignited in a mixture with potassium chlorate. The strong light is due to the fact that in spite of the great heat of its combustion the oxid produced is neither melted nor vaporized, but glows as incandescent solid particles.

The position assigned to sodium in the potassium family belongs to magnesium in the calcium group. It is found in more natural compounds than calcium, and differs from it more than calcium does from strontium and barium. The taste of all its soluble salts shows that its ion is bitter.

Magnesium Hydroxid, $Mg(OH)_2$.—When a solution of magnesium sulphate or chlorid is treated with excess of sodium or potassium hydroxid, a white gelatinous precipitate separates. A trace of it dissolves and turns red litmus blue. In solution of ammonium chlorid or other ammonium salt the magnesia dissolves. The dry $Mg(HO)_2$ is a white powder which, on being heated, loses water, changing to magnesium oxid.

Magnesium Oxid, MgO (*Magnesia*).—This is best prepared by heating the light carbonate. A white, fine, bulky, and light powder is produced, called *calcined magnesia*. It is tasteless, odorless, and, though almost insoluble in water, it still turns moist litmus-paper blue. On standing with 15 parts of water for half an hour it becomes hydrated to a gelatinous magma. It is used as an antacid and antidote. Dose: 5 to 60 gr. (0.32–3.88 gm.). It is a component of *ferri hydroxidum cum magnesii oxido*, the antidote for arsenic (p. 270).

Magnesii Oxidum Ponderosum.—Heavy *magnesia* is made by calcining the heavier variety of carbonate. It is a white, fine, dense powder which does not gelatinize in water and is slower in action than light magnesia, though it corresponds to it in other respects. The dose is the same.

Magnesium chlorid, $MgCl_2$, is a deliquescent salt formed by the action of hydrochloric acid on the oxid or carbonate. It is present in various bitter, saline mineral waters, to which it imparts a laxative property.

Magnesium carbonate, $MgCO_3$ (*normal* or *neutral carbonate*), is formed by passing carbon dioxid through a mixture of water and the basic carbonate.

Magnesii Carbonas (U. S. P.) $(MgCO_3)_4$, $Mg(OH)_2 \cdot 5H_2O$.—When a solution of magnesium sulphate or chlorid is boiled with one of sodium carbonate, CO_2 is evolved and a white gelatinous precipitate forms, which is a varying mixture of carbonate

and hydroxid.[1] If the solution be dilute and cold, very little CO_2 is evolved. The deposit is white, light, and bulky, and is called *magnesii carbonas levis*, or *magnesia alba*. It is mostly $MgCO_3$, neutral carbonate. If the solution used be concentrated and hot, and the water be boiled off, a denser product is obtained, containing some hydroxid, and called *magnesii carbonas ponderosus*. This is sometimes dispensed in large cubes. Both forms are white, light, faintly earthy in taste, and insoluble in water. They neutralize the acids of indigestion and the corrosive acid poisons.

Magnesii bicarbonas (*fluid magnesia*) is a solution of the carbonate in water charged with carbon dioxid. It is alkaline and bitter in taste.

Mistura magnesiæ et asafœtidæ (*Dewees' carminative*) contains the carbonate, tincture asafetida, tincture opium, sugar, and water. It is given for flatulent diarrhea. Dose: 1 to 4 fl. dr. (3.75–15.00 c.c.).

Magnesium sulphate, $MgSO_4.7H_2O$ (*Epsom salt*), occurs in sea-waters and in waters of bitter saline mineral springs. The salt is prepared by the action of sulphuric acid on magnesium carbonate, prismatic or acicular crystals forming, which are freely soluble and neutral, with a cool bitter taste. It is a favorite cathartic when free watery discharges are desired. The purged fluid flows from the vessels into the intestines by osmotic pressure. To mask the bitter taste possessed by the soluble magnesium salts, effervescing solutions are used, in which carbon dioxid is liberated from a carbonate by the action of citric acid.

Magnesii sulphas effervescens is a granular mixture of magnesium sulphate and sodium bicarbonate with tartaric and citric acids. Dissolved in sweetened water the CO_2 set free masks the bitter taste of the sulphate.

Liquor Magnesii Citratis (*Effervescing Citrate of Magnesia*).—This is a palatable solution, quickly mixed and tightly stoppered so as to retain the carbon dioxid. It contains magnesium carbonate, citric acid, syrup, potassium bicarbonate, and water. Dose as a cathartic: 2 to 8 fl. oz. (60–236 c.c.).

Detection of Magnesia.—The ion magnesium is divalent and colorless, like that of calcium. Its carbonate, like that of other alkaline earths, is insoluble in water, but unlike the others, soluble in ammonium salts like the chlorid. Hence, to separate it from them, ammonium chlorid is added to the suspected solution until it ceases to precipitate with ammonium hydroxid.

[1] In another place (p. 228) it has been stated that the alkaline carbonates are split by solution in water forming some hydroxid which turns red litmus blue. Magnesion, $Mg+$, is thrown down by both the anions $(CO_3)^-$ and $(HO)^-$ thus formed by hydrolysis.

If now ammonium carbonate be added, carbonates of calcium, strontium, and barium are precipitated, leaving magnesium in solution. After filtration a solution of disodium phosphate is added to the filtrate. There being ammonia present already, there is deposited a crystalline precipitate of ammonium magnesium phosphate, $MgNH_4PO_4$. All the heavy metals must have been separated first by hydrogen sulphid or ammonium sulphid. There is no characteristic color to the magnesium flame.

STRONTIUM

Symbol, Sr. Atomic weight, 87.62.

This metal and barium are more closely allied to calcium than is magnesium, just as cesium and rubidium resemble potassium more than does sodium. They are much rarer than calcium and magnesium and have little medical interest, though barium figures as a poison because of its employment in pyrotechnics. Strontium is found in nature combined in its sulphate, *celestite*, and in its carbonate, *strontianite*. The metal is obtained readily by electrolysis of its fused chlorid. It is yellowish, rather tough, like calcium, unites with oxygen in the air, and reacts energetically with water, evolving hydrogen. Its ion, Sr^{++}, is divalent and behaves so much like calcion that it is not worth while to consider its salts in detail. The *bromid*, *iodid*, and *salicylate* are official and are used in medicine with essentially the same indications as the corresponding salts of potassium. The chief use is in the making of fireworks, growing out of the beautiful dark-red color of its flame. Its detection depends on the fact that it is the only substance that gives this flame reaction. The spectrum shows lines in the red, orange-red, and blue.

BARIUM

Symbol, Ba. Atomic weight, 137.37.

Occurrence.—This metal occurs in nature as the sulphate, *barite*, and as the carbonate, *witherite*. It is obtained by passing the electric current through the fused chlorid.

Properties.—It is a white metal resembling calcium and strontium in that it oxidizes in the air and reacts energetically with water. Its ion Ba^{++}, is divalent, colorless, and poisonous. It is recognized by the heavy white precipitate with sulphuric acid and the sulphates, and by the yellowish-green color of its flame.

The *hydroxid*, $Ba(HO)_2$, or *baryta water*, is more soluble and more basic than lime-water, and is used to neutralize acids and test for carbon dioxid, which precipitates the white carbonate.

$$\underset{\text{Barium hydroxid.}}{Ba(OH)_2} + CO_2 = \underset{\text{Barium carbonate.}}{BaCO_3} + H_2O.$$

The soluble salts, *barium nitrate*, $Ba(NO_3)_2$, and *barium chlorid*, $BaCl_2$, are used as reagents for precipitating sulphanion, SO_4'', in barium sulphate, the most insoluble of sulphates and of barium salts:

$$Ba^{++}, (NO_3)^-, (NO_3)^- + K^+, K^+, (SO_4)^= = 2K^+, (NO_3)^- + BaSO_4.$$

As fast as barion is neutralized by the union with the sulphanion, $BaSO_4$ is precipitated, insoluble, and therefore undissociated. Because of its resistance to acids and solvents it wears well as a pigment under the name "permanent white." Freed from soluble salts, the pure sulphate is used as a shadow-forming medium in Röntgen-ray examinations of stomach and intestines.

Certain salts of barium used in pyrotechny, in wood-staining, and in glass-making sometimes figure in toxicology as irritant poisons which, when absorbed, cause cardiac depression and convulsions. The *chlorid* and the *nitrate* occur in white, soluble crystals resembling the ordinary purgative "salts," for which they have been taken by mistake. White insoluble *barium carbonate* is present with arsenic in "Rough on Rats."

Symptoms.—Gastro-intestinal irritation is shown by vomiting and diarrhea, with straining and abdominal pain. After absorption dilation of the pupils with convulsions, paralysis, and heart failure may supervene.

Fatal Dose.—About 100 gr. (6.5 gm.) of the chlorid proved fatal to a woman, although by gradually increasing the daily quantity, Pivondi was enabled to take in divided doses 119 gr. (7.7 gm.) in a day.

Fatal Period.—Death occurred in one case in one hour, in another case in fifteen hours, in another case in thirty-four hours, and again as late as a week after taking the poison.

Treatment.—The best chemical antidote is magnesium sulphate (Epsom salts) or sodium sulphate (Glauber's salts). Both have the power to precipitate the barium as insoluble sulphate. The stomach should then be washed out with milk and water. Anodynes are indicated for pain; heat and stimulants for the cardiac depression.

Post-mortem Appearances.—Any or all of the signs of gastro-intestinal inflammation may be present—*i. e.*, patches of redness, swelling, softening, effusions, ulcerations, and even perforation.

Experiments on rabbits show that after chronic poisoning for thirty days all the organs contain barium—the bones most of all, the kidneys, brain, and spinal cord show a less amount, the liver still less, and traces only are in the lungs, heart, and muscles.

Tests.—1. *Dilute sulphuric acid* precipitates barium sulphate, which is insoluble in hydrochloric or nitric acid.

2. *Neutral potassium chromate* gives a yellow precipitate, insoluble in water, but soluble in hydrochloric or nitric acid.

3. A green hue is given to a colorless flame when a barium salt is held in it by a loop of platinum wire moistened with hydrochloric acid.

Detection.—Having dissolved the organic matter by hydrochloric acid and potassium chlorate and precipitated most of the common metals by hydrogen sulphid and ammonium sulphid, the filtrate is treated with ammonium carbonate, which precipitates barium, strontium, and calcium carbonates. This precipitate is dissolved in nitric acid and dried until the free acid is driven off. The residue is treated with equal parts of absolute alcohol and ether, which dissolve calcium nitrate, but leave the others undissolved. The calcium solution gives a white precipitate to sulphuric acid. The residue, dissolved in water and treated with a little acetic acid and potassium chromate, gives a yellow precipitate of barium chromate. The filtrate, treated with ammonium carbonate and ammonia, gives a white precipitate of strontium carbonate.

By another method the organic matter may be burnt, the ash fused with sodium carbonate, dissolved in hydrochloric acid, and tested as stated above.

RADIUM

Symbol, Ra. Atomic weight, 226.4.

A white and brilliant metal of the alkaline earths, closely related to barium.

Occurrence.—Radium is found in excessively minute quantities in *carnotite* and in *pitchblende*, a black mineral found in Colorado, Texas, and Bohemia; minerals rich in uranium.

Preparation.—By tedious and difficult processes of fractional crystallization a ton of pitchblende will yield $1\frac{1}{2}$ gr. (0.1 gm.) of radium chlorid. By electrolysis with a mercury anode, this yields radium amalgam, which on distillation in hydrogen separates the pure silvery-white metal, radium. It decomposes and dissolves in water and oxidizes in air, but as chlorid or bromid forms a permanent salt.

Physical Properties.—Radium chlorid $RaCl_2$, containing 76 per cent. radium, is obtained as small, colorless, self-luminous crystals. It burns with a brilliant red light, which gives a characteristic spectrum of vivid lines. While the nearly pure salt is obtainable by costly and tedious processes, the product in the market is a mixture of it with barium chlorid in variable proportions. It is sold, however, by its radium content, as determined by electroscopic and photographic tests. From its properties an atomic weight for the metal has been

deduced of 226.4. This is the third highest known; the two elements above it in weight, uranium and thorium, have the same remarkable property of radio-activity.

Radio-activity is a property first discovered by Becquerel in the uranium salts obtained from pitchblende. They emit spontaneously invisible radiations, which penetrate opaque substances and show their presence by blackening sensitive photograph films and by conducting away, through the air, the charge of electrified bodies. The rays from the electrified current streaming from the cathode of a Crookes vacuum tube, and the Röntgen rays given off from the glass of that tube when bombarded by radiant matter, have these properties; but the rays of polonium, uranium, thorium, and radium are produced incessantly and irresistibly without the outside stimulus of electric excitement. Radium has radio-activity intensified 2,000,000 times beyond the standard fixed by uranium. The radium emission, like that of the Crookes tube, is sufficiently intense to produce fluorescence in barium platinocyanid, which is not the case with the rays from uranium and thorium.

The intensity of this radiating action is measured definitely by the rate of leakage of electricity in a certain period, from a charged gold-leaf electroscope, due to the increased conductivity of a given quantity of air caused by the "ionizing" influence of the emitted rays. The unit of intensity is the radio-activity of uranium. Thus, when it is said that a sample of radium salt has a radio-activity of 5000, it is meant that the rays emitted by the sample raise the conductivity of the air 5000 times as much as would an equal weight of uranium.

Radium emits three kinds of *rays* and a radio-active gaseous *emanation*. The three rays are named α (*alpha*) or *ionic*, β (*beta*) or *cathodic*, and γ (*gamma*) or *æthereal*, like the Röntgen rays.

The *alpha* species consist of atoms of helium of twice the mass of hydrogen atoms; they are charged positively, are projected with a velocity of about 20,000 miles per second, can be deflected by a magnet, are readily absorbed by surrounding objects, have little penetrative power, and ionize gases so that electrified bodies near by are rapidly discharged. They emit heat and burn the skin.

The *beta* species are flying electrons, one seventeen-hundredth the weight of a hydrogen atom; they are negatively charged, strongly affect the silver salts of a photographic plate, traverse glass and many opaque solid partitions, and are influenced by a magnet; all 100 times more strongly than the *alpha* rays.

The *gamma* species, like waves in the æther, move in straight paths, are neutral electrically, are not deflected by a magnet, and penetrate most substances, even thin plates of lead, powerfully. They are considered to be identical with the irregular and intense

pulses of the Röntgen rays emitted from the high vacuum Crookes' tube when excited by electricity, and are therapeutically the most useful.

The *emanation* or *Niton* yields radium and helium; it wells forth as a luminous gas, slowly, without ceasing, imparting feeble luminosity to any body it may touch. In a dark room it can be seen, by its luminosity, to be subject to draughts, to flow inside glass tubes, to penetrate cotton-wool, sulphuric acid, and thin metallic foil, but to be stopped by mica. It is unaffected by all chemical reagents, but is condensed by low temperatures. Its boiling-point is $-150°$ C. ($-238°$ F.). It imparts temporary radio-activity to surrounding objects, apparently by a deposit of invisible powder so minute that in years the accumulation would not be weighable. Neutral electrically, it can ionize other gases so as to disperse electric charges. Even when confined with the utmost care, in a month it disappears entirely, no matter if it be hermetically sealed. The colored bands characteristic of the *emanation spectrum* are seen in a few days to show the yellow-green line typical of helium, and eventually the lines are those of helium throughout. If the emanation be dissolved in water it generates the gas neon, if dissolved in a solution of copper sulphate it generates argon, but in neither liquid is helium a product of the disintegration. It has medicinal effects like those of the element, but not to the same degree.

Quantities and concentrations of radium emanation are expressed in terms of "curies" and Mache units. A "curie" is the amount of emanation in equilibrium with 1 gm. of radium; a microcurie, one-millionth of a "curie," is the amount of emanation in equilibrium with 0.001 mg. radium and is equivalent to about 2500 Mache units.

Heat Radiation.—Pure radium chlorid, without cessation and for an indefinite period, evolves heat enough to maintain itself at a constant temperature of 1.5° C. (2.7° F.) above other objects in the room. A gram weight gives off 100 *calories* every hour, an amount sufficient to raise 1 gm. of ice-water to the boiling-point. In a year the amount of energy put forth is enormous, and yet the loss of weight is so infinitesimal that the most delicate balance will not indicate it. The heat results from the atomic collisions.

Transmutation.—The rate of emission is unlike that of a chemical process in that it is unaltered by change of temperature. Even the cooling by immersion in frozen hydrogen has no effect. The heat given off in the disintegration of radium is a million times as much as that of its combustion or of any chemical process. There are two main groups of true radio-elements: (1) the series formed by the disintegration of uranium, and (2) the series of similar products from thorium. Together they include 28 well-

defined radio-elements, of which only the parents uranium and thorium were known before the use of radio-active methods. Lineally descended by the spontaneous breaking up of uranium are ten elements: uranium X, ionium, radium, radium-emanation, radiums A, B, C, D, E, and F. Uranium is the progenitor of a third subgroup of six radio-elements—actinium, radio-actinium, actinium-emanation, and actiniums A, B, and C. The thorium series (2) includes a similar progeny of ten successive elements, among which are to be noted mesothorium and thorium-emanation.

Induced Radio-activity.—If a sealed tube containing radium be immersed for a day in normal salt solution and then removed, the solution contains the emanation and for a few days shows all the radio-active powers, though in a lower degree, which diminishes rapidly.

Chemical Properties.—The emitted rays convert oxygen into ozone and change yellow phosphorus to red. The *alpha* rays immediately coagulate a sensitive solution of globulin. The *beta* and *gamma* rays liberate iodin from iodoform in the presence of oxygen.

Physiologic Effects.—Under the influence of the rays, nutrition is profoundly modified, the development of growing animals arrested, and after prolonged exposure some are killed. Radium chlorid, when uncovered at a short distance, soon inflames the skin, producing painless ulcers; the partially blind are enabled to see luminous appearances, and by its injurious effects upon the nervous system it induces paralysis and death. Applied directly to the part in a lead tube to filter off the *alpha* and *beta rays*, thereby using only the *gamma* rays which penetrate lead, it breaks up superficial cancers and growths, like lupus, rodent ulcer, and the hypertrophied thyroid of goiter. The pathologic tissues are more sensitive to it than normal tissues. For this purpose at least 1 mg. of 1,000,000 activity is required. As it destroys bacteria, it has been hoped that inhalation of the emanation or some radio-active vapor will prove helpful in tuberculosis of the lung. The emanation is also efficient, but for a few days only. The high cost of radium has brought into notice mesothorium, which has virtues akin if not equal to those of radium. It loses in radio-activity after ten years, whereas radium lasts for thousands of years. The emanation locally applied relieves neuralgic and rheumatic pains.

Intra-atomic Matter.—Viewed in the light of recent discoveries, the picture of the constitution of substance—the atomic theory—has its details better defined than ever and made more true to nature. The notion that matter is *granular* or *atomic* still subsists, as it rests upon the necessity of chemistry for separate combining units which are centers of force. But the physical integrity of the chemical atom can no longer be main-

tained. Through the highly exhausted vacuum of a Crookes tube negative electricity streams in electrons of radiant matter, which are neither molecules nor atoms. These *cathode rays* are convection currents of electricity, like the stream of ions in liquid electrolytes, but differ from them in having carriers 1700 times less massive than the hydrogen atom. "The negatively electrified particles have the same charge and the same mass, whatever be the nature of the gas in the tube or the nature of the electrode. They therefore form an invariable constituent of the atoms and molecules of all gases, and presumably of all liquids and solids" (Thomson).

The **electron theory** assumes that electric conduction is the property of intra-atomic units of negative electricity which are detached from the atoms. The atom may be considered as an open structure with vacant spaces relatively large and a cluster of these much smaller electrons in swift gyration within the relatively enormous atomic space, controlled by electric forces which normally in the aggregate are neutral. The chemical characteristics of the atom are due to its mass, which is proportional to the number of its electrons. The ions of solutions are atoms carrying more or less of these electrons than belong to them in their normal or neutral state. If an atom gains an electron, the atom becomes negatively charged, if it loses one, it becomes positively charged. When a molecule of NaCl dissociates, the Na^+ atom surrenders an electron to the Cl^- and their neutrality is lost. Valency is electric in character. The electropositive univalent atom, such as hydrogen, engaged in a chemical action becomes ionized on losing one electron. The electronegative univalent ion, such as chlorin, becomes stable when it loses one electron. The divalent positive oxygen atom becomes an ion in gaining two electrons, and so on. Valency on this hypothesis is an effect of the number of electrons that can get free from or are caught up by the aggregation of electrons which constitute the particular kind of atom. Radio-activity is an effect of perturbations of the intra-atomic forces and a subversion of the normal system, which is attended by the loss of energy emitted in rays, the disintegration of the atom, and such transmutations of substances as are seen in the radium *emanations* (p. 249).

Radio-activity Common.—Many ordinary things are found to be radio-active in an exceedingly minute degree, such as ground air from cellars and caves and newly fallen snow and rain, surface waters and that of mineral springs, tinfoil, glass, silver, lead, copper, zinc, aluminium, platinum. But marked radio-activity is a property of the elements of heavy atomic weight only.

The degree in which bodies are transparent to Röntgen rays, to

cathode rays, to the rays sent out by radio-active substances, and also the nature of the secondary rays emitted by different elements are all determined by the atomic weight of the element.

III.—THE EARTH METALS

ALUMINIUM

Symbol, Al. Atomic weight, 27.1.

Occurrence.—This is the only element belonging to the group of metals of the earths which is at all common or which has any practical value. It ranks next to oxygen and silicon in abundance and is of great importance, whereas the others are exceedingly rare and of little interest. The members of this group, aluminium, scandium, yttrium, lanthanum, gallium, ytterbium, etc., all form trivalent ions. Aluminium silicate is not only a constituent of many crystalline rocks, but is also the chief component of clays and slates. Nearly all minerals, except sandstone and limestone, are ore beds of it. Every brick has nearly a pound of this metal in it. A native aluminium silicate is official under the name of *kaolinum.* It is a soft, white powder, clay-like in taste, insoluble in water. It is used in making pill masses and also in the *cataplasma kaolini,* U. S. P., which contains kaolin, boric acid, thymol, methyl salicylate, oil of peppermint, and glycerin. It is used as an antiseptic, hygroscopic, plastic dressing.

Preparation.—Aluminium oxid is fused in iron crucibles by the heat of the electric current, which then decomposes it, the metal seeking the cathode container, and the oxygen uniting with the carbon anode to form carbon monoxid. To obtain fusion at a lower temperature *cryolite,* a double fluorid of aluminium and sodium, is first melted as a bath in which the oxid fuses and breaks up and the used-up oxid of aluminium is replaced as the process requires.

Properties.—Aluminium is a bluish-white, silvery metal, changing very little on exposure to the air. It is protected from deep rust by an imperceptibly thin film of oxid, which quickly forms and firmly adheres. It can be drawn into hair-like wire and beaten into very thin *leaf* for "silvering." As it does not blacken, like silver, and is extremely light (specific gravity 2.7), it is often used for household ware. Melting at 700° C. (1292° F.), it is easily molded. It is a good conductor of heat and electricity. Its drawbacks are its softness, its inability to resist the action of salt solutions, and its solubility in alkalis. At high temperatures it combines with oxygen, giving a brilliant light

and great heat. Two alloys of great stability are in use: *aluminium bronze,* which is golden yellow, and *magnalium,* white; the latter contains about 10 per cent. of magnesium.

It is attacked and dissolved by acids:

$$Al \quad + \quad 3HCl \quad = \quad AlCl_3 \quad + \quad 3H.$$

The ion of aluminium is trivalent, Al^{+++}, and colorless, forming salts which are astringent and soluble. These salts when dissolved resemble the alkaline carbonates in that they are split up by water into the hydroxid and acid. The hydroxid being a weak base, the hydrion of the strong acid makes the reaction acid, thus:

$$AlCl_3 \quad + \quad 3H_2O \quad = \quad Al(OH)_3 \quad + \quad 3HCl.$$

The proof of this dissociation of $AlCl_3$ is found in the fact that the original salt is not obtained when the water is evaporated.

Aluminium hydroxid, $Al(OH)_3$, *hydrated alumina,* is formed as a gelatinous precipitate from solution of aluminium salts on the addition of a small quantity of an alkali or alkaline carbonate.

$$Al_2(SO_4)_3 \quad + \quad 6NH_4OH \quad = \quad 3(NH_4)_2SO_4 \quad + \quad 2Al(OH)_3.$$

If the liquid contain suspended particles or coloring-matter, these are carried down, and give a color to the dried precipitate, which, under the term *lake,* is used as a pigment. *Aluminii hydroxidum* (U. S. P.) is a light, white, amorphous powder, without taste, wholly insoluble in water or alcohol, but soluble in strong acids or alkaline solutions. Dose: 3 to 15 gr. (0.2–1.0 gm.).

When heated to redness the hydroxid changes to oxid:

$$2Al(OH)_3 \quad = \quad Al_2O_3 \quad + \quad 3H_2O.$$

The hydroxid is weakly basic, forming with acids three kinds of salts, according as one, two, or three hydroxyl groups are replaced by the acid ions. Although precipitated by caustic potash or soda in small amounts, the precipitate dissolves in excess of these alkalis, forming soluble aluminates. Metallic aluminium dissolves in the caustic potash or soda, with the formation of aluminate and the evolution of hydrogen:

$$3KHO \quad + \quad Al \quad = \quad K_3AlO_3 \quad + \quad 3H.$$

This reaction shows that its hydroxid, AlO_3H_3, acts in this case as an acid, splitting off acid hydrogen from its hydroxyl groups. Like a tribasic acid, it yields three anions, $(H_2AlO_3)'$, $(HAlO_3)''$, and $(AlO_3)'''$. Neither the acid nor basic quality can be strong in a substance which plays either part according to circumstances.

Much concentration of the acid-hydrogen ion and the basic-hydroxyl ion would cause the formation of undissociated water, as when a strong base and acid meet. Unlike the magnesium salts, aluminium hydroxid is not soluble in excess of ammonia. The absence of solvent power is due to the weak basicity of ammonia.

Aluminium hydroxid is so weakly basic that it does not take carbonic acid from the air or water. No carbonate is ever formed, but the silicate is carried suspended as a fine powder by rivers and deposited in quiet waters as clay.

Aluminium oxid, Al_2O_3, *alumina*, occurs nearly pure in nature as a hard mineral *corundum*. *Sapphire* is a blue and *ruby* is a red variety, colored by admixture of cobalt or chromium. When obtained by calcining the hydroxid it is a light, white, odorless powder, which fuses at a high heat and forms hard crystals on cooling. A hard granular variety, colored dark by iron oxid, is known as *emery*.

Aluminium chlorid, $AlCl_3$, is prepared by the action of hydrochloric acid on aluminium hydroxid. It is a very hygroscopic, white crystal, used in organic chemistry with mixtures of a hydrogen compound and a chlorin compound, to promote the union of the hydrogen of one with the chlorin of the other, and causing the residues to combine in a synthetic compound.

Aluminium sulphate, $Al_2(SO_4)_3 + 18H_2O$, is prepared by heating aluminium silicate or aluminium hydroxid with sulphuric acid. It is a white crystalline powder, freely soluble in water and insoluble in alcohol. It is used in medicine as a local astringent. Owing to the weakness of aluminium hydroxid as a base, this, like the other salts, is hydrolyzed by water, so that an appreciable per cent. of hydrion causes it to react acid. This salt is used as the acid factor in some baking powders (see p. 229). It does not crystallize so well as alum, but by using pure materials in its manufacture better results are obtained than formerly.

Alum (*Alumen*, U. S. P.).—This name was first applied to the double sulphate of aluminium and potassium, $AlK(SO_4)_2$, $12H_2O$. Mixed in the right proportions, solutions of potassium sulphate and aluminium sulphate will form beautiful regular octahedra with a sweetish astringent taste and acid reaction. It is soluble in water, but insoluble in alcohol. Dose: 10 to 15 gr. (0.66–1.00 gm.).

Common alum is a type of a large series of isomorphous salts, which are double sulphates of alkaline metals and aluminium or some member of the iron group. A univalent and a trivalent metal replace the four atoms of hydrogen in $2(H_2SO_4)$.

Ammonium ferric alum is $NH_4Fe(SO_4)_2.12H_2O$.

Potassium chromium alum is $KCr(SO_4)_2.12H_2O$.

Alumen Exsiccatum (*Dried* or *Burnt Alum*).—The effect of heat on alum is first to melt the crystals and next to drive off the water, leaving a spongy white mass, which is slowly soluble in water, with a local astringent and mild caustic effect on animal tissues.

Toxicology.—Alum coagulates albumin and pepsin and retards the peristaltic movements of the bowels, thus arresting digestion. When absorbed, it constricts the capillaries, lessening mucous secretions, and stopping hemorrhages from capillary vessels. It is a prompt irritant emetic, and has so many incompatibles that it is best given alone.

Excessive doses of this salt have produced irritant symptoms, sometimes ending in death. Medicolegal interest in aluminium is mainly limited to the question of its action when used as a constituent of certain baking-powders which are consumed by the ton in domestic bread-making. In these powders sodium bicarbonate furnishes gaseous carbon dioxid, which is liberated by the action of aluminium sulphate, leaving in the bread sodium sulphate and aluminium hydroxid. The fact that many thousands of persons use these powders without any perceptible injury, local or systemic, apparently indicates that the insoluble aluminium hydroxid is unabsorbed, or if changed to a soluble chlorid by the gastric juice, the amount absorbed must be within the limits of toleration by many persons. At the same time it is proper to note that large doses of alum given to dogs subcutaneously cause paralysis of sensation and motion, with fatty degeneration of the liver and kidneys. The safest view is to hold aluminium salts an unnecessary addition to bread, and certainly of no value as food. Their presence in any but the smallest amount should be considered proof of adulteration and the article excluded from the foods considered wholesome.

Domestic filters are often fitted with attachments for adding alum to the raw and more or less muddy water, with a view to causing the formation of gelatinous aluminium hydroxid, which entangles the mud and some bacteria in a precipitate that will not pass the sand or other porous media. The amount of alum required varies from 1 to 10 gr. in the gallon, according to the turbidity of the water and the amount of dissolved carbonates with which to react. Using judgment, the proportion of alum may be kept within the limits of the precipitation, and thus no dissolved alum pass into the filtered water.

Detection.—Having incinerated the organic matter in a platinum dish, the ash should be treated with hydrochloric acid, excess of acid removed by heat, a few drops of nitric acid added, and a final solution in hydrochloric acid boiled and filtered.

This *acid* solution is not changed by potassium ferrocyanid or hydrogen sulphid, as are solutions containing the heavy metals. Its hydroxid is precipitated from an *alkaline* solution by hydrogen sulphid, or from a neutral solution by ammonium sulphid. With potassium hydroxid a white precipitate falls, redissolved by excess, whereas an excess of the reagent does not affect the precipitate from a solution of the alkaline earths. With ammonium hydroxid a white precipitate is formed insoluble in excess.

Logwood Test.—The most convenient test for alum in *bread* is made with a freshly prepared tincture of logwood. This tincture is made by digesting 5 gm. of freshly cut logwood chips with 100 c.c. of alcohol. Having diluted 5 c.c. of the logwood tincture with 90 c.c. of water and added 5 c.c. of saturated solution of ammonium carbonate, the mixture is *immediately* poured over 10 gm. of bread in a glass dish. After five minutes the liquid is poured off, the bread slightly washed, and dried at 100°C. A lavender or dark-blue color denotes that alum is present. Pure bread is at first reddish, fading to a yellow or light brown.

Delicacy.—This test yields a distinct blue with 0.02 per cent. of alum, or 7 gr. in a 4-lb. loaf.

Fallacy.—Several other mineral adulterants produce a somewhat similar reaction.

Alum in Drinking Water.—When *excess* of alum is used in filtering water its presence may be detected by the logwood test as follows: To the suspected water add fresh tincture of logwood, enough to give a decided color; now add a solution of ammonium carbonate. If a blue precipitate fall, then alum is present at least 1 : 1000; if no precipitate, but a blue color persist for an hour, then alum is present at least 1 : 50,000. If before the hour be out the color be brown or pink, then there is no alum.

Aluminium Sulphate in Baking Powder.—A small quantity of the suspected powder is burnt to an ash, which is then treated with boiling water and filtered. If the filtrate yields a flocculent precipitate when treated with ammonium chlorid, then aluminium is present in the sample.

WATER SUPPLY

MINERAL WATERS

While natural waters usually contain mineral constituents in varying proportions, some are so rich in dissolved salts and gases as to have a marked taste and a medicinal effect. These spring saline waters are grouped according to some important component, as saline, carbonated, chalybeate, alkaline, sulphurous.

Saline.—Among these may be named Kissingen, Saratoga, Seidlitz, Hot Springs of Arkansas. They contain chlorids, sulphates, and carbonates of sodium, potassium, lithium, magnesium, and calcium.

Carbonated.—The best known of these are Apollinaris, Selters, and Old Sweet West Virginia. They effervesce with the carbon dioxid, which while dissolved enables them to hold in solution carbonates of sodium, magnesium, and calcium.

Sulphurous.—Prominent among these are White Sulphur, W. Va.; Sharon, N. Y.; Blue Lick, Ky. They sparkle with the dissolved gases, carbon dioxid and hydrogen sulphid, and hold in solution chlorids, sulphates, and carbonates of sodium, potassium, magnesium, calcium, and sometimes iron.

Alkaline.—Familiar examples are seen in Gettysburg, Pa.; Hot Springs, Va.; Buffalo Lithia, Va.; and Vichy, France. They contain a large amount of sodium carbonate and lesser amounts of chlorids, sulphates, and carbonates of sodium and other metals.

Chalybeate.—Among well-known iron springs may be mentioned Cresson, Pa.; Rockbridge, Va.; Bath Alum, Va. They owe their tonic virtues to the iron sulphate, carbonate, and oxid held in solution by the dissolved carbon dioxid. They also contain sodium, magnesium, and aluminium compounds.

WATER FOR DOMESTIC USE

Water of absolute *chemical* purity is not found in nature, and probably would not be desirable for drinking purposes. Distilled water is not palatable; it lacks the ions to which we have grown accustomed and which are necessary to health. The natural supplies that are preferred instinctively contain a moderate amount of mineral matter and some carbon dioxid in solution. Water that is *hygienically* pure is of the first importance to communities and individuals. It must be palatable, clear, contain not more than 15 parts of harmless minerals in 100,000 of water, with no lead or other poisons, and be wholly free from the specific bacteria of disease.

Rain water is the primary form of nature, and if it be collected in the country and stored in well-made cisterns, is wholesome. It may have dissolved from the air traces of ammonia and other gases and in the city it may wash down dust particles, some of which are organic and bacterial, though in most cases the microorganisms are not disease-producing. Rain water is only relatively pure.

Surface Water.—Rain water falling upon the earth becomes in part surface water, flowing and remaining above ground. The

lie of the land causes it to collect in ponds or lakes or to drain away in creeks and rivers. In agricultural watersheds the erosion by the water increases materially the organic matter, the increase being dissolved from decaying vegetation. The mineral addition, however, is very small, and the water remains almost as soft as rain water. If the watershed be thickly inhabited, as along the banks of some rivers, it may remain wholesome as long as it is free from the specific bacteria of disease. Such a water is liable at any time to be contaminated by the entrance of bacteria from sewage containing excrement from cases of typhoid fever, dysentery, cholera, or diphtheria. The evidence is incontrovertible that drinking water can cause these diseases, and that it does so, because of the presence of the peculiar germs. In the cholera epidemic of Hamburg, Germany, in 1893, the typhoid-fever outbreak of Plymouth, Pa., in 1883, and of Ithaca, N. Y., in 1903, the dejecta of a single patient passing into the water supply were sufficient to cause an enormous amount of mischief.

Ground-water is that part of the rainfall which sinks through the porous earth until it is stopped by a bed of clay or rock. The water then moves laterally upon this impervious stratum through the permeable soil toward the nearest surface water at a lower level. This addition by diluting a river lessens the proportion of sewage material that the river may have received. Sometimes it comes forth again as a natural spring; sometimes it is tapped by a well. On its way through the porous soil it dissolves out the soluble minerals, but by a natural filtration such water is free from organic matter and wholesome, provided it has not taken up too much mineral salts to be palatable. Its organic purity is due to the fact that it has traversed the home of the non-pathogenic bacteria which abide in the surface zone of the earth and form a gelatinous layer. Decaying organic matter, surface water, and the air furnish the bacteria with their food. By the time the water has descended eight or ten feet it has been so exhausted of organic matter that it no longer supports the life of micro-organisms. Ordinary house wells are sometimes contaminated and become foci of infection. The mode of access of the germs to a well may be by communication from a near cesspit through a gravelly stratum, or by the loss of the natural filtration powers of the soil through saturation with filth resulting from old and crowded communities.

The pollution of domestic wells is not only by underground channels, but also by overflow of foul surface water from barns or drains. Deep wells in rural districts give wholesome water if properly curbed and covered, and not sunk too near cesspits, drains, and stables.

Hard and Soft Waters.—As a rule, surface waters are said to be *soft* and well waters of a limestone region *hard*. *Hard waters* are so named because in rinsing the hands, after soaping them, the water does not clean away from the pores that which gave a hard feeling left after washing. This disagreeable residue is made up of the insoluble curds of calcium and magnesium oleate, resulting from a reaction between the sodium oleate of soap and the salts of magnesium and calcium in the water. Until these salts are all precipitated as oleate the water and the soap are useless detergents, for only then do they form a lather. By boiling a hard water carbon dioxid is driven off and the soluble calcium and magnesium bicarbonates converted into insoluble carbonates, which are precipitated. This process *softens* the water by removal of the *temporary hardness*. The salts remaining in solution, such as the sulphates and chlorids, after boiling give to the water its *permanent hardness*. In laundries it is customary to soften water and add to its cleansing powers by the addition of *concentrated lye*, sodium hydroxid; or *pearlash*, potassium carbonate. These precipitate the calcium and magnesium salts and give to the water greater penetrating and dissolving power over grease, epithelial débris, and other dirt.

DRINKING WATER

Sand Filters.—**Artificial improvement of the house supply** is commonly obtained by filtering the water through sand in domestic filters, aided by the precipitation of suspended matter with alum, as described on p. 256. This yields a specimen much improved in appearance and in taste, but not with certainty deprived of the germs of communicable disease (p. 261).

Artificial improvement of a town supply is best done after the methods of nature. To obtain water like that of springs and deep wells for a town or city it is slowly filtered through sand. In this way it is purified precisely as is rainfall on passing through porous earth. Beds of sand are constructed and thoroughly underdrained. The water is permitted to spread over the surface and percolate through the sand. In a short while a bacterial jelly forms on the surface which performs the same work of purification as is done for spring and well waters by the nitrifying bacteria that crowd the superficial layers of the earth. The high efficiency of slow-working sand filters has been demonstrated beyond question. Of many examples, that of the neighboring cities, Altona and Hamburg, in Germany, is most celebrated.

These two cities are both dependent upon the river Elbe for their water supply, but the Hamburg intake is above the city,

while that for Altona is below Hamburg, *after it has received the sewage of* 800,000 *persons.* In 1893, in Hamburg, the deaths from cholera amounted to 1250 per 100,000, and in Altona to but 22 per 100,000 of the population. The epidemic spread from the Hamburg side up to the boundary line between the two cities and there stopped. In one street which separates them *the Hamburg side was stricken with cholera, whilst that belonging to Altona remained free.* In those houses supplied with the Hamburg water cholera was rife, while in those furnished with the Altona water not one case occurred. The Hamburg water, to start with, was comparitively pure when contrasted with the dilute sewage drawn

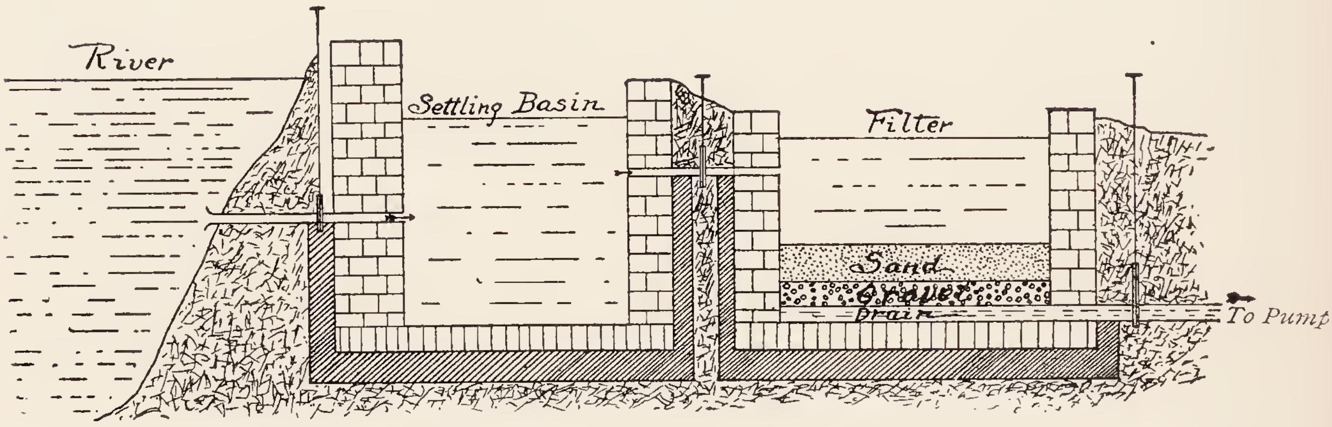


FIG. 61.—Cross-section of filter plant (Jour. A. M. A.).

from the Elbe by Altona, but, in the latter case, the water was submitted to filtration through sand, while in Hamburg the water was in its raw condition as drawn from the river.

Construction of a Town Filter.—The unit filter is a water-tight masonry reservoir with an area of one-half to two acres. On the floor of the reservoir are perforated underdrains, upon which are placed layers of coke or crushed stone and gravel of increasing fineness, and last of all a bed of sand 2 to 4 feet deep, which is to embody the bacterial jelly. It is highly desirable to have a settling basin, through which the raw water must pass before it is permitted to flow upon the filter, after leaving its mud behind.

Storage.—The method of nature in purifying *surface* waters which do not penetrate the porous soil is quiescence, as in the case of lakes and ponds. A running stream has very little power of self-improvement. A public supply may be drawn from a creek or river and stored in reservoirs, leaving it to the ripening effects of time. The longer it is stored, the greater the opportunity afforded the nitrifying bacteria to destroy the organic matter necessary for the sustenance of the germs of disease. The total number of bacteria in a surface water is much reduced by storage for a while and by slow filtration through sand after. The best results in purifying the water and reducing the mortality are obtained by using both storage and filtration.

In case it is impossible to have the water supply treated as indicated above, decided improvement can be had by installing small *filters* in houses. These make the water clear, and if properly constructed and cared for, lessen the number of bacteria. If neglected they become breeding grounds for bacteria and fail to be of benefit. The only filters that are recommended are those which force the water through porcelain, such as the Pasteur and the Berkfeld. The porcelain tubes should be cleaned every week or so, and boiled in water for half an hour. It is well to bake them in a pottery furnace fire every six months.

When the drinking water of a household comes under suspicion it should be condemned as raw water, since it can be made wholesome by boiling only. Most of the bacteria are killed at the boiling-point, but some survive unless the boiling be continued for twenty minutes. When thus sterilized the water may be recharged with air by a bellows or it may be poured from pitcher to pitcher. It may also be drunk as a weak infusion of tea or lemonade to make it palatable.

When traveling or in camp it may be most convenient to use chlorinated lime as a sterilizing agent on a small scale. Mixed with an equal amount of sodium chlorid to prevent clumping it is added to contaminated water in the proportion of 0.5 gm. per liter. After ten minutes the chlorin taste is removed by neutralizing with sodium bicarbonate or thiosulphate. Five minutes later, effervescence ceases and the precipitated lime is filtered out. The experience of over one hundred American cities using this hypochlorite treatment on a large scale shows it to be efficient and economic, yielding drinking water clear, palatable, and free from disease germs.

Examination of Drinking Water.—While chemical analysis is not without some importance, especially if no other knowledge be obtainable, the most significant facts about a water supply are often obtained by an engineer's inspection of the watershed and the surroundings of the reservoir. Every shallow well in a densely populated district is unsafe and should be condemned. No chemical or bacterial examination is required to determine the fact of sewage contamination when drains are seen to enter the stream. Any water supply which has once received polluted material may, under like conditions, be again contaminated. If it be under suspicion, special survey of the territory will often point out the particular source of mischief.

The constitution of ground and surface waters is different even when both may be wholesome. The organic matter revealed by chemical and bacterial tests applied to a surface water does not necessarily condemn it, but would be significant of pollution if found in a well water. Correct interpretation of the analysis

depends upon a knowledge of the source of the sample as well as the mode of collection and transportation.

Biologic Test.—Reliance is fairly well placed upon this test properly performed by experts trained in the procedures of the bacteriologic laboratory which cannot be adequately presented in this work. An approved method is based upon the fact that, though there may not be present in the specimen the typhoid bacillus or other pathogenic bacteria, there is reason to condemn the water when the intestinal organism *Bacillus coli communis*, by its presence, witnesses to sewage contamination. Absence of this bacillus, after careful search, would indicate that there is no direct access of animal or human feces to the well or other source of water supply.

When sewage is diluted with distilled water, and the mixture tested, it has been found that the biologic test will show the presence of the *Bacillus coli*, when the proportion of sewage was so small that chemical analysis revealed nothing suspicious. It must be recognized that proper bacteriologic methods surpass the chemical both in delicacy and in indicating sewage pollution. When such evidence is not at hand resort may be had to the following chemical tests.

The value of these quantitative results depends mainly upon a comparison with previous analyses made of the same water under normal conditions.

The **total solids** are determined by weighing a platinum or nickel evaporating dish, filling it with 1 L. of the water, and evaporating over a water-bath, drying at 110° C. (230° F.) or over H_2SO_4, and weighing dish and residue. On heating to redness, charring of the residue would indicate organic matter. The total solids should not exceed 500 mg. per liter.

Chlorids in themselves are not dangerous, but are significant because the sodium chlorid of wells and rivers is mainly derived from urine and other domestic waste. A sudden increase in the proportion of chlorids points to an access of sewage. In titrating for chlorids 100 c.c. of the suspected water is put in a beaker, made neutral or alkaline with a drop of sodium hydrate, and colored with neutral potassium chromate. Silver nitrate solution is run in from a buret until a red color persists. The test solution contains $AgNO_3$, 4.79 gm. per liter, and each cubic centimeter = 0.01 gm. of chlorin per liter (0.7 gr. per gallon). In an emergency a water should be condemned which shows more than .03 gm. per liter (3 gr. per gallon), or which reveals marked increase from its normal amount, as determined by previous examinations.

Organic Matter by Permanganate Process.—The presence of organic contamination is revealed by the change of color in

a pink solution of potassium permanganate. It loses oxygen and is reduced to a faintly brownish product.

Experiment 1.—Put in a beaker 100 c.c. of pure distilled water, add 5 c.c. of dilute sulphuric acid, boil on wire gauze and add 5 drops of dilute permanganate solution (30 mg. in 100 c.c.) and boil 5 minutes. There is no fading of color. Now add urine or egg albumin and boil again; the color is discharged. The number of cubic centimeters of a standard pink solution required to overcome this fading of color is a measure of organic impurity.

Ammonia is a characteristic product of the decomposition of nitrogenous organic matter, such as urea, and its presence in amounts in excess of 0.05 mg. per liter is a danger signal indicative of sewage pollution. The *free ammonia* is obtained by distilling the suspected water after adding to it some sodium carbonate, leaving a remainder in the flask for the next process.

Some of the nitrogenous matter of animal origin may be present unchanged, and to obtain proof of this it is necessary to break it up and separate the nitrogen as *albuminoid ammonia*. This is done by distilling the remainder after subjecting it to the action of an alkaline permanganate solution. Pure drinking water does not yield more than 0.1 mg. per liter.

The determination of ammonia in the distillate is made by the comparison of the yellow color produced by *Nessler's solution*,[1] when measured amounts are added to the water, and to a solution of ammonium chlorid of known strength. The elaborate part of this operation is the distillation. It may be dispensed with if *free* ammonia only is to be determined, the Nesslerizing being applied to the original sample after precipitating the calcium salts with sodium carbonate (one part in ten million of water is detected by the yellow color).

Experiment 2.—Measure 50 c.c. of suspected water in a test-tube and add 2 c.c. of Nessler's solution. Look down through the tube at a piece of white paper to note if the depth of color equals that obtained from a solution of ammonium chlorid of known strength. If more than a trace of ammonia is present a precipitate falls. The presence of *nitrates* and *nitrites* is no longer regarded as evidence against the sanitary purity of water, as their source may be harmless. Traces are discovered as the result of oxidation of harmless constituents. The following test has great delicacy.

Experiment 3.—Make the reagent first by dissolving 0.5 gm. of sulphanilic acid in 150 c.c. of acetic acid (25 per cent.) and

[1] This is an alkaline mercuric potassium iodid solution made by dissolving 5 gm. of potassium iodid in hot water and adding a solution of 2.5 gm. of mercuric chlorid in 10 c.c. of hot water. The red mixture clears when there is added 16 gm. of potassium hydroxid in 40 c.c. of water and the whole diluted to make 100 c.c.

mixing this with a solution of 0.1 gm. of naphthylamin in 200 c.c. of acetic acid. Keep in the dark. Of this reagent put 2 c.c. in a well-cleaned beaker with 50 c.c. of water. If nitrites are present 0.01 mg. will give a pink color and larger quantities a rose-red.

The details of water analysis are too elaborate to be considered in this place. They can be found in works devoted to that subject alone or to sanitary chemistry in general.

IV.—THE ARSENIC GROUP

ARSENIC (Arsenum)

Symbol, As. Atomic weight, 74.96.

THE element arsenic is considered among the metals because its analytic reactions resemble those of antimony and tin, whose sulphids are insoluble in dilute acids, but soluble in alkalies and in ammonium sulphid. In its chemical affinities it is allied to phosphorus so closely that with good reason it might have been studied among the non-metals or acid-formers. Its oxids, like those of phosphorus, behave as anhydrids of acids. In the following table resemblances of trivalence and pentavalence are shown, which include non-metallic phosphorus with its highly developed acid-forming properties; arsenic, a weak acid-former, and antimony, which forms both acids and bases:

	Hydrids.	Chlorids.	Oxids.	Acids.	Sulphids.
P	PH_3	PCl_3	P_2O_3 — P_2O_5	H_3PO_3 — H_3PO_4	P_2S_3.
As	AsH_3	$AsCl_3$	As_2O_3 — As_2O_5	H_3AsO_3 — H_3AsO_4	As_2S_3.
Sb	SbH_3	$SbCl_3$	Sb_2O_3 — Sb_2O_5		Sb_2S_3.

All three are irritants and have salts that are poisonous, both locally and by their depressing systemic effects.

Poisoning by some arsenic compound is often resorted to by the secret homicide, and comes under notice of the courts more frequently than any other form. Taking suicides and homicides together, it has caused more deaths than any other poison except opium and its derivatives. During the seventeenth century a strong solution of white arsenic, known as *aqua tophana*, was widely employed by the poisoners of Italy and France, who were convicted only by self-confession. In spite of the fact that modern chemistry finds it the easiest of all poisons to detect, it is still used not only by suicides, but by criminals, many of whom escape punishment for years. Within a period of eighteen months Mrs. Robinson of Somerville, Mass., assisted by a quack doctor who knew something about arsenic, poisoned in succession five persons

of her own family without exciting suspicion until her sixth victim died. Of 8 deaths of trusting friends laid to her charge, arsenic was found in the cadavers of 6. Mrs. Sherman of New Haven, Conn., succeeded in escaping suspicion while she killed, successively, 3 husbands and 8 other persons of her immediate household with arsenic. The peculiar death of her fourth husband led to her conviction.

A case of wholesale poisoning in Havre was revealed by a commission of four experts appointed to decide if certain premises used as a drug shop were unsanitary. They reported that the symptoms of chronic ill-health ascribed to the state of the house were in reality due to arsenic poisoning. It was then discovered that a clerk, in the course of two years, without exciting suspicion, had poisoned 15 persons, 3 of them fatally. They that survived, after severe disturbance of the digestive, cutaneous, and respiratory organs, were left more or less completely paralyzed.

White arsenic, or *ratsbane*, is a favorite poison because it is cheap, can be bought as a vermin-killer at any drug-store in the United States, and, owing to its very feeble taste, can be mixed with the food without the victim recognizing the foreign ingredient. The acute symptoms simulate indigestion or *cholera morbus*, and thus the physician is misled. It is the practice of undertakers to inject sodium arsenate or other arsenic preparations into the viscera of a corpse to prevent decay. This places an insuperable difficulty in the way of conviction, and knowledge of this fact must often embolden the criminal. In the absence of rigid restrictions upon the sale of arsenic compounds, such as are imposed by other governments, the United States has a bad eminence in the number of fatal cases of arsenic poisoning.

Arsenum or Arsenicum.—Free or elementary arsenic is a steel-black mineral with a metallic appearance, when oxygen is excluded, subliming at 400° C. (752° F.), and when burned in air, at 180° C. (356° F.), emitting an odor of garlic. It is an ingredient of some "fly-powders." It is present in commercial zinc, iron, and sulphuric acid. It makes a hard alloy with lead, is used in the manufacture of shot, and is often found in Brittania metal. The insolubility of the element as found in these alloys protects us from poisoning by them. Arsenic has been found to be the cause of the poisoning induced by eating sardines that had been put up in a soldered tin box. The liability of tin and solder to contain arsenic leads to the regulation of the French Commission of Hygiene that tin should not contain more arsenic than 0.01 in 100.

In testing, it appears as a black stain on copper in Reinsch's test, and as a brown stain on porcelain, and a mirror-like ring on

glass tubing in Marsh's test. It oxidizes by exposure to the air, and in that state becomes poisonous. When volatilized by heat it readily unites with oxygen of the air and forms the poisonous vapor of white arsenic, As_2O_3 (Fig. 67 *a*).

Arsenic Terhydrid (AsH_3) (*Arseniuretted Hydrogen*, *Arsin*, *Arsonia*).—This is a gas generated by the action of nascent hydrogen on reducible arsenic compounds. A hydrogen generator containing zinc is supplied with dilute sulphuric acid and the arsenic solution is added after the hydrogen has filled the apparatus:

$$3Zn + 3H_2SO_4 + \underset{\text{Arsenous acid.}}{H_3AsO_3} = \underset{\text{Zinc sulphate.}}{3ZnSO_4} + 3H_2O + \underset{\text{Arsenic terhydrid.}}{AsH_3}$$

The gas is colorless, has an odor of garlic, and burns into water and arsenic trioxid:

$$2AsH_3 + 3O_2 = As_2O_3 + 3H_2O.$$

The flame is bluish white or livid, and if a cold body, such as porcelain, is put into it, the metallic arsenic is deposited as a brown-black spot. The gas, in its course through a small glass tube heated to redness, decomposes and leaves its metallic element condensed on the colder part of the tube as a mirror-like ring. Arsin has a reducing action upon solutions of silver nitrate, causing a black deposit of the metallic silver and liberating arsenous acid. It is the most deadly of the inorganic compounds of arsenic. In addition to the early symptoms—nausea, shivering, dizziness, and prostration—in the severe cases more serious effects appear. There may be jaundice, with dark-colored blood, the urine may be bloody and suppressed, and coma supervene, ending in death.

Arsenic trichlorid, $AsCl_3$, can be prepared by burning arsenic in a current of chlorin. It is a heavy colorless liquid which boils at 134° C. (273° F.) and is volatile at lower temperatures. Hydrochloric acid converts part of arsenic trioxid into chlorid and dissolves it. On distilling this solution the arsenic chlorid is found in the distillate. By simple evaporation some of this chlorid is volatilized and lost. But if arsenic trioxid or arsenous acid be converted into arsenic acid by some oxidizing agent, the arsenic acid will not be changed to volatile chlorid by the action of hydrochloric acid. Arsenic chlorid is highly poisonous.

Arsenic Trioxid (As_2O_3) (*Arsenious Oxid*, *Arsenic*, *White Arsenic*, *Ratsbane*).—Besides the above common names for *Arseni Trioxidum*, it has another, incorrect, but once official, *acidum arsenosum*. When dissolved in water it gives a faintly acid reaction because it changes to *arsenous acid*, according to the equation: $As_2O_3 + 3H_2O = 2H_3AsO_3$. This compound, H_3AsO_3, cannot be

obtained in the solid state, existing only in solution. Three classes of its salts are known according as to whether one, two, or three of the hydrogen ions have been replaced by a metal. By losing the elements of water it forms meta-arsenous acid, which exists in salts known as meta-arsenites, $H_3AsO_3 = H_2O + HAsO_2$. By roasting its ores arsenic trioxid can be obtained as minute octahedral crystals, as a smooth, heavy powder, or as irregular masses having the appearance of translucent glass and white porcelain. The cake of condensed vapor is at first amorphous and semitransparent, and is then called *vitreous*; later, by absorption of moisture, it turns to the white, crystalline, opaque, *porcelain-like* variety which has different solubility. The shops usually dispense it as a heavy white powder, partly amorphous, partly crystalline, prepared from the vitreous variety by grinding. The crystalline "flowers of arsenic" obtained by subliming and condensation are made up of octahedral crystals entirely. Samples of the powder from different packages vary in microscopic appearance, and a specimen may often be identified by the size, luster, and relative proportion of the crystals it contains. The taste is so faint and lacking in distinctness as to be unnoticed when mixed with food. While it is sparingly soluble in water, and less so in liquid foods, such as milk, beer, coffee, it may easily be suspended in thick soups or incorporated with bread as a solid.

It is extremely unlikely that As_2O_3 can be taken into the stomach in solution and afterward revert to the solid form.

Owing to the difference in relative amounts of the two forms present in different samples, it is not possible to state the solubility in precise terms, but usually 1 fl. oz. of cold water will dissolve from $\frac{1}{2}$ to $\frac{3}{4}$ gr. (about 1 : 1000). A permanent solution of 16 gr. to the fluidounce (about 30 : 1000) can be made by boiling water with it for an hour. In spite of the greater weight (specific gravity, 3.699), powdered arsenic has the curious property of floating on water as a white film. By adding hydrochloric or nitric acid, or by making the water alkaline with the hydroxids or carbonates of the alkalis, the arsenic readily dissolves without change of color. White arsenic has no odor, but if heated on charcoal it is reduced to metallic arsenic, which in vapor has an odor of garlic.

Physiologic Effects.—In the vast majority of cases the local action of arsenic is pronounced. It does not corrode dead and living tissue alike, as would the corrosive acids and alkalis. Vital irritability is required, or the effect on organic matter will be small. Applied to a part, it irritates so profoundly that the phenomena of inflammation appear at once and make rapid progress to the latest stage of local death. It blisters the skin like a burn,

and the mucous surfaces respond with equal promptness to its inflaming touch. The widespread inflammation of the stomach and bowels accounts for numerous cases of rapid death, but the greater number of fatal cases do not exhibit sufficient local mischief to explain the prostration of nervous energy which ends in death. To account for the fatty degeneration of important organs, such as the heart, liver, and kidneys, the theory has been broached that cell protoplasm yields oxygen to arsenous acid, converting it into arsenic acid, and later it reverses its action, reducing the arsenic acid. These unwonted activities induce the morbid changes referred to.

Medical Uses.—Arsenic is much used in medicine as a general tonic for malarial affections and diseases of the skin and nervous system. It is given either alone or in combination with remedies of the same class. The dose is $\frac{1}{64}$ to $\frac{1}{12}$ gr. (0.001–0.005 gm.).

A mode of administration often practised is to give 5 drops of the *liquor acidi arsenosi* (U. S. P.) or of *liquor potassii arsenitis* (U. S. P.) (Fowler's solution), well diluted, after meals, increasing the dose 1 drop daily until the disease is under control or until the eyelids puff and the bowels move too freely, or faint, darting pains are felt in the abdomen. The dose is then reduced to a safer quantity, and persisted in until the warning returns, when it is again reduced. All this time the arsenic pervades all the tissues and can be found in the urine. Occasionally persons are encountered who have an idiosyncrasy for arsenic. Even the minimum dose will produce unpleasant effects.

It sometimes happens that the early warnings are ignored and the arsenic persisted in until permanent injury is done. The usual form of injury is neuritis causing paralysis, local or complete.

The *incompatibles* of arsenic trioxid are lime-water, tannic acid, cinchona, the vegetable astringents, and most metallic salts.

Symptoms.—If the poison be taken in solution and the stomach be empty, the symptoms may appear in eight minutes. If taken solid and with a meal they may be delayed for as long as ten hours. The usual interval before the first signs is from half an hour to an hour. If a fatal dose has been taken, the symptoms produced are many and various. Departures from the typical forms are frequent, and no symptoms can be considered as characteristic.

In *acute* poisoning, the patient dying within twenty-four hours, the symptoms usually come on within an hour. They are those of a violent irritant producing local inflammation. Added to these, and sometimes occurring independently, are the phenomena of collapse and coma, due to the profound involvement of the central nervous system. The capillaries of the gastro-intestinal

tract dilate enormously, become more permeable, and permit the escape of the blood-serum which occasions "rice-water" stools. The accumulation of the blood in the vessels of the abdomen and the loss of blood-plasma tend to bring on collapse and muscular cramps.

The most conspicuous signs are: (1) An excruciating pain in the pit of the stomach, aggravated by pressure (this burning pain is sometimes absent); (2) sinking sensations and nausea accompany or may precede the pain; (3) dry mouth, sore throat, and urgent thirst are common, but may be absent; (4) persistent and forcible vomiting, a sign of an irritability that cannot support the blandest drinks: after ejecting the food the stomach throws off a rice-water fluid and, later on, a thick mucus, sometimes brown from bile and sometimes streaked with blood; (5) purging and straining at stools, which may be fetid and bloody, but are apt at first to be thin and watery, like those of cholera morbus (this purging may be absent or insignificant, and in some cases there is obstinate constipation); (6) the urine may be red, bloody, albuminous, scanty, and even suppressed; (7) a feeble, frequent, and irregular pulse ushers in the other symptoms of collapse, the livid and anxious face, sunken eyes, cold and clammy skin; (8) cramps in the calves of the legs, restlessness, spasms ending in unconsciousness.

A small proportion of the cases are classed as *nervous* or *cerebral*, because the central nervous system is prominently affected, while the local irritant symptoms, such as vomiting and purging, are slight or wholly absent. The conspicuous nervous phenomena are great prostration, stupor, convulsions, paralysis, collapse, and death in coma.

A *subacute* form is one favored by ingenious criminals who give the poison in small doses, repeated at intervals, so as to cause death by gradual prostration through stages relatively slow. The symptoms make their onset later and are less violent than those of the typical acute form. Most of the cases are of this variety; sooner or later there will be loss of appetite, fainting sensations, nausea, dry throat, retching, shooting pains referred to the stomach and intestines, and diarrhea. These merge into vomiting, great abdominal tenderness, tenesmus with bloody stools, scanty and albuminous urine, jaundice, eczema or erythema, nervous weakness, feelings of numbness and tingling in the extremities, muscular pains, cramps, paralysis, convulsions, and coma.

Under proper treatment the acute symptoms may subside, and some days or even weeks afterward sequelæ will appear. These are attributable to a chronic inflammation of the peripheral nerves, ending in degeneration of the fibers extending from the periphery

toward the center, causing loss of sensibility and paralysis in the hands or feet, which may progress until the muscles waste and give the electric response known as the reaction of degeneration.

Anomalous Cases.—Emphasis should be placed upon the statement above, that no symptoms can be considered characteristic. Fatal cases have been reported which presented typic postmortem appearances, and yet during life exhibited no pain, vomiting, or purging, and in which thirst was not marked in degree.

Fatal Dose.—Two grains is the smallest fatal dose of white arsenic yet reported. Suicide was accomplished in the case of a woman who had recently aborted, by taking ½ fl. oz. of Fowler's solution, equal to 2 gr. of arsenic trioxid, in broken doses, within four days. Three grains of absorbed arsenic would probably prove fatal to an average man.

Recovery is possible after much larger quantities, as the symptoms vary according to the bodily condition of the person, the state of the stomach, and the form of the poison. Remarkable recovery may ensue if the poison is taken in lumps or if vomiting evacuates the stomach before absorption has set in.

Fatal Period.—The shortest interval before death is twenty minutes. A large dose may overwhelm the entire nervous system, so as to bring about collapse and coma within the hour. The average period is about twenty-four hours. In the subacute cases the fatal termination may not occur for several weeks.

Treatment.—The first indication is to *evacuate the stomach* by administering an emetic mixture of a teaspoonful of mustard and a tablespoonful of salt in a tumbler of warm water. This may be repeated in ten minutes, or hypodermic injection (5 drops of a 2 per cent. solution) of apomorphin, or an emetic dose of sulphate of zinc can be given. Where criminal poisoning is suspected, tartar emetic should be avoided, as it will make detection of arsenic more difficult. The stomach-tube will prove valuable if the stomach be not full of mixed food, pieces of which would occlude the openings in the tube. Large drafts of hot milk and water will facilitate the washing out of the poison. At the same time the antidote may be given to make the residue insoluble and inert. For this purpose reliance is placed on teaspoonful doses of dialyzed iron or on the freshly made *moist ferric hydroxid,* to convert the arsenous acid into ferric arsenite, which is only very sparingly soluble (p. 342).

$$\underset{\text{Ferric hydroxid.}}{Fe(HO)_3} + \underset{\text{Arsenous acid.}}{H_3AsO_3} = \underset{\text{Ferric arsenite.}}{FeAsO_3} + 3H_2O.$$

In the official preparation, *ferri hydroxidum cum magnesii oxido* (U. S. P.), two antidotes are combined. This may be prepared extemporaneously by diluting ½ oz. of *tinctura ferri chloridi*

with a tumbler of water and adding magnesia in excess. The whole mixture may be taken without straining and repeated several times. The arsenous acid forms insoluble ferric and magnesium arsenites. If the ferric hydroxid be prepared by adding ammonia water to ferric sulphate or ferric chlorid, then the gelatinous precipitate should be separated from the excess of ammonia by straining through a handkerchief or piece of cheesecloth. To clear the intestine a dose of castor oil should be given. In spite of evacuants and antidote it sometimes happens that the poison in the form of a powder adheres unchanged to the folds of the mucous membrane.

Postmortem Appearances.—Putrefactive change is usually retarded when the body is permeated with arsenic. If the dose has been large and life prolonged until absorption could take place, this preservative effect will often keep the viscera free from gases and putrid odors for as long as seventeen months. A smaller dose, especially if rapidly followed by death before general diffusion could occur, would not have the same action. The pathologic changes induced are usually those of gastro-enteritis common to the class of local irritants of the stomach and bowels, and if the patient should survive for a number of hours, the absorbed poison will set up fatty degeneration of the heart, liver, and kidneys.

Mouth, Pharynx, and Esophagus.—The repeated acts of vomiting bring the poison up from the stomach more or less dissolved and active. Inflammatory change sets in at once, and the upper part of the alimentary tract will present enlarged vessels, reddened patches, and erosions.

Stomach.—The lining membrane of the stomach may be covered with a tough mucus or lymph in which white particles of the poison will be imbedded, or, if Paris green has been taken, there may be patches of a bright green color. Sometimes the arsenic penetrating the gastric walls as far as the peritoneum has been turned into yellow sulphid by the reaction with hydrogen sulphid of putrefaction. The mucus itself may be abundant and dark, containing blood. Small dark red dots of effused blood, looking like flea-bites, may stud the surface of the membrane, itself a paler red, obviously due to diffused inflammation. Upon the prominent folds of the mucous membrane these effusions may run together in well-marked streaks of dark-red color. The inflammation may involve the other coats of the stomach, and all of them be found thickened and corrugated. Occasionally, localized gangrene ensues. Rarely does the inflammation progress to ulceration, and still more rarely does the ulcer involve the whole structure, causing perforation.

While some degree of gastric inflammation will nearly always

be found, it is important to note that death may occur from the cerebral effects ending in coma, while the mischief done to the stomach may be insignificant.

Intestines.—If death be delayed for several days, the whole length of the intestinal tract may be inflamed, but usually the small intestine, and more frequently the duodenum, alone will be involved. There is diffused redness, with scattered patches of a deeper hue, and the contents may be bloody, or perhaps yellow from the formation of yellow sulphid. Like the stomach, the intestines may show little or no sign of inflammation, even with the arsenic present in considerable amount, the death being due to the effect on the central nervous system.

Changes in remote parts may occur if life be prolonged for a number of hours, and are most conspicuous in the *heart*, *liver*, and *kidneys*. Any or all of these may show fatty degeneration. The heart is the seat of effusions of blood under the endocardium, especially of the left ventricle.

Chronic Poisoning.—Peculiar features are found in chronic poisoning that have given rise to the theory that arsenic is *cumulative*. Careful investigation shows that the poison is not stored up in the tissues for such a length of time as are lead and mercury, though the effects appear to accumulate in force and gravity.

Arsenic is readily diffusible and, passing to the tissues, abides for a few weeks and then is eliminated. The dose may be considerable, yet if the patient lives for three weeks the arsenic may have entirely disappeared from the soft tissues, but may still be detected in the bones. On the other hand, cases are recorded where the poison has been found in the liver and bones after two and even six months.

The poison has been known to enter by many avenues—inhaled by the lungs, swallowed in food or as excessive medication, applied to the skin by mistake in cosmetics or in the red dye of socks and gloves. The person falls into "poor health," losing appetite and all desire for exertion. Soon twinges of pain, especially sudden colic, will appear. Complaint is made of "sickness" and faintness. The eyelids puff, the conjunctiva is reddened, and the eyes become very sensitive to light. Such signs of indigestion as occasional vomiting, colic, and chronic diarrhea arise. The color fades from the face, the complexion becoming waxy. The person is said to have a wasting fever. Progressive weakness and loss of weight prevail throughout. The hair becomes dry and may fall out, and the nails are brittle and loose. The skin may exfoliate or show spots of darker hue, with eruptions of eczema or erythema. The mouth may lose patches of mucous membrane, form ulcers, and show the symptoms of salivation.

The throat, nose, larynx, and bronchial tubes may be affected with a catarrh, causing cough, bloody expectoration, aphonia, and copious coryza. At a later period the nerve-fibers become inflamed and degeneration of this structure is a consequence. At first the sensory nerves indicate the mischief going on by attacks of numbness and tingling in the extremities, which are followed eventually by total absence of normal sensation, or, it may be, by pain and tenderness. When the motor nerves of the hands and feet are involved there are loss of power in them and wasting of the affected muscles. Even if the poison is discontinued, the paralysis usually lasts for many months, recovery being very slow and generally incomplete. The paralysis may extend until it is general, and death ensue from failure of the heart due to fatty degeneration. A horny condition of the palms and soles, or keratosis, may be produced by the long-continued use of arsenic as a remedy in chronic psoriasis.

Arsenic Applications.—Deaths have been recorded from applications of arsenic, with homicidal intent, to the rectum and the vagina. It has poisoned when used as an urethral injection.

In these cases of absorption from other mucous surfaces and also when applied to the unbroken skin, as ointment, lotion, or powder, the symptoms are much the same as when taken into the stomach. There is, first, a local inflammation, soon followed by nausea, vomiting, thirst, abdominal pain, diarrhea, suppressed urine, and nervous symptoms.

An arsenic ointment applied to the scalp of a child to cure an eruption caused death in ten days, with symptoms of gastro-enteritis. By mistake white arsenic was dispensed for a dusting-powder to the skin, with fatal consequences to 17 children. Arsenic plasters used to remove tumors have had severe systemic effects, and even death has been caused by them. In such cases the poison has been found to be distributed throughout the body.

Arsenic-eating.—It has been proved indubitably that in Styria, Lower Austria, and India individuals have been found who, by carefully increasing the dose at long intervals, have accustomed themselves to take with impunity what in others would produce poisonous symptoms.

These arsenic-eaters take for twenty or thirty years from $\frac{1}{2}$ to 2 gr. or even more of arsenic trioxid at intervals of once a week or oftener, with the intent to increase their powers of endurance. The persons examined have been robust men who lead an active mountain-climbing life. It is not unlikely that to a high constitutional power of resistance they add an unusual activity of the excretory organs, an acquired impermeability of the absorbing membranes. They appear to be especially liable to sudden death.

Popular writers have helped to create the impression that there are village communities who indulge themselves in arsenic as others do in tobacco. This is not well founded, nor is there evidence to support the opinion that moderate arsenic-taking is common among persons who wish to improve their complexion. Among its transient pathologic effects are a clear pallor, sometimes a circumscribed flushing of the cheeks, and a glistening of the eye. These soon pass into a waxy skin and puffy eyelids—anything but pleasing to look upon. Very rarely it happens that a person for whom Fowler's solution has been prescribed will take it of his own volition to restore his health, but a persistence in the habit is soon found to be prejudicial and the dose given up. Physicians consider it doubtful if any considerable number of persons find it compatible with comfort for more than a brief period.

Tests for Arsenic in the Solid Form.[1]—When undissolved, it is easy to recognize the poison by heating it in a sublimation tube and applying other tests to the deposited vapor.

Sublimation Test.—Arsenic trioxid sublimes without fusing at a temperature lower than 218° C. (424° F.), the sublimate under a lens presenting octahedra and modified forms, such as tetrahedra and dodecahedra (Fig. 62, *c*).

Fallacies.—The octahedral form distinguishes the minute arsenic crystals from other volatile white solids subliming at this temperature, such as corrosive sublimate, calomel, and oxalic acid. While many authorities assert that the sublimate of antimony oxid is always amorphous, according to others it may sometimes occur as octahedral crystals like arsenic.

Reduction Test.—This test is applied to any solid compound of arsenic, including Paris green, the two sulphids, and any arsenite. The dry substance is introduced into a reduction tube, part of which has been drawn out to a small caliber at the bottom. It is covered with six times the quantity of a well-dried mixture of 3 parts of sodium carbonate to 1 part of potassium cyanid. Heated

[1] The duty of the physician in attendance, who suspects poison during life, is to examine the vomited matters, urine, or feces by some test such as Reinsch's. Having discovered arsenic, if the case ends fatally, he should inform the state prosecutor and insist on a post-mortem which, if possible, should be held in the presence of the chemical expert. Having tied the esophagus just above and the intestines just below the stomach, another ligature is applied at the lower end of the gut and the whole tract between with contents is removed without opening. The stomach and intestines are then put in a clean new jar with glass stopper, sealed with paraffin and fastened by sealed cords. In the same way the brain is sealed up in a separate jar and in another jar the liver, spleen, kidneys, and a piece of muscular tissue. Any urine in the bladder or vomited matters must be put in clean new bottles.

The sealed containers must be kept locked up until delivered to the chemist by the physician.

gently, some moisture may first appear on the tube. This can be removed with a spiral of filter-paper, a swab of absorbent cotton, or by gently heating the moist glass. When the tube is dry, strong heat is applied to the flux and then to the arsenic. The arsenic compound is reduced to metallic arsenic, which is deposited higher up on the tube as a mirror-like ring, black shading to brown or gray (Fig. 62, *a* and *b*).

Fallacies.—The compounds of antimony yield no mirror with this flux, but the compounds of mercury, cadmium, tellurium, and selenium may. When viewed by a lens the mercury mirror is found to have a fringe of globules. To distinguish the arsenic mirror the end of the tube must be broken off and the ring heated

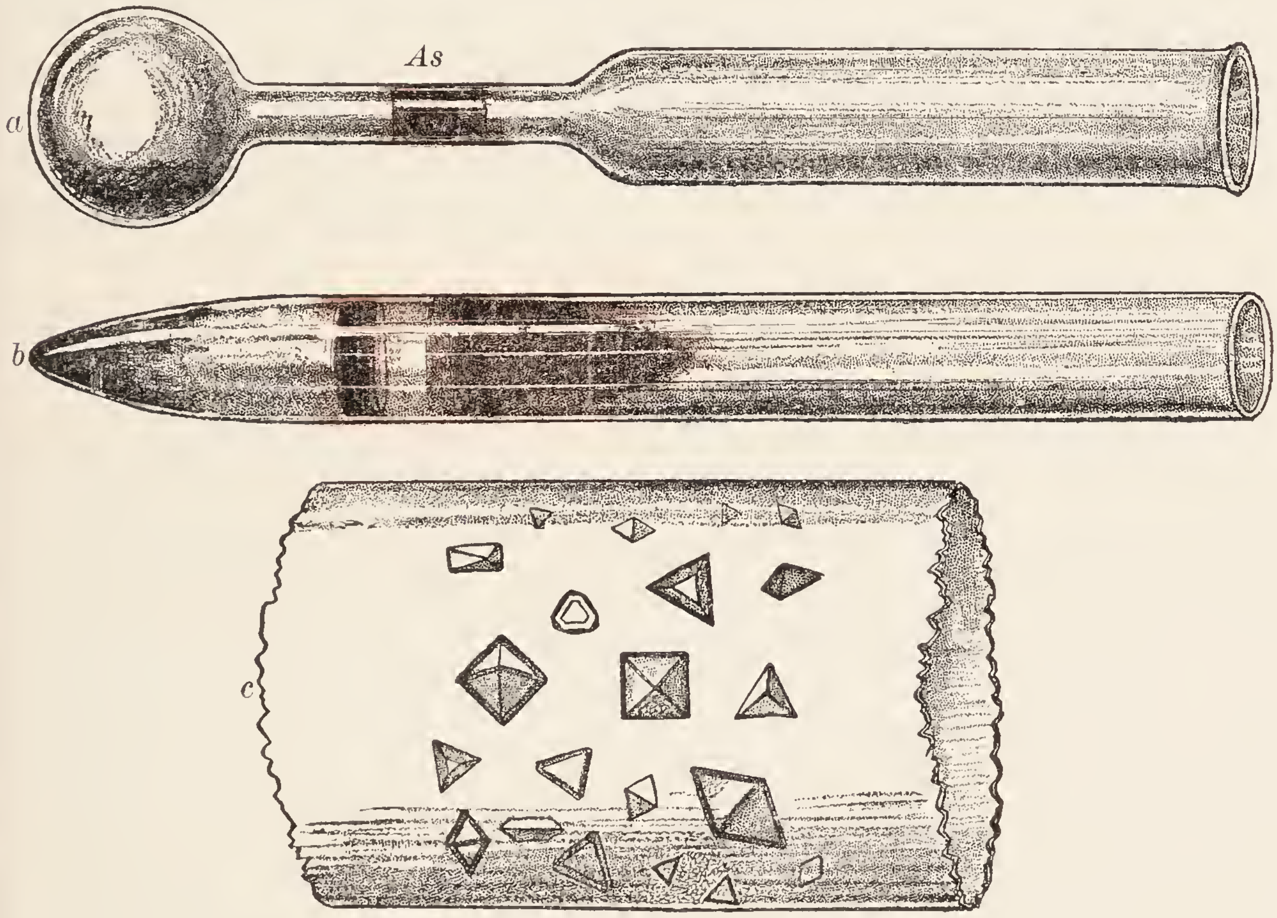


Fig. 62.—*a* and *b* are two reduction tubes showing arsenic mirror after reduction test; *c*, octahedra of As_2O_3 sublimate, magnified.

with the tube aslant. The air playing over the hot arsenic will oxidize it, and the mirror will be vaporized and appear on the cooler parts of the tube as minute white crystals of arsenic trioxid, octahedral in form (Fig. 62, *c*). If another specimen is treated with a warm solution of chlorinated lime, the mirror will dissolve in a manner characteristic of arsenic.

Delicacy.—If $\frac{1}{1000}$ gr. of arsenic be tested in a tube contracted to $\frac{1}{20}$ in. in diameter, it yields a visible sublimate which will re-sublime and show many crystals of arsenic trioxid.

Tests for Arsenic in Simple Solutions.—When the poison has been obtained in solution free from organic or other matter, the following tests will help to identify it:

Ammoniosulphate of Copper Test.—Enough of the reagents for the test can be freshly made by putting about 5 drops of ammonium hydroxid in a test-tube and diluting it with 10 c.c. (3 fl. dr.) of water. To this dilute ammonia-water a weak solution of copper sulphate is added until the bluish-white precipitate ceases to dissolve. The slight excess of cupric hydroxid should be removed by filtration. The clear-blue solution added to a solution of arsenic trioxid will throw down a bright-green precipitate of cupric arsenite, $CuHAsO_3$ (*Scheele's green*) (Plate 2, No. 2). A portion treated with ammonium hydroxid dissolves as a clear-blue liquid; another portion will make a colorless solution with nitric acid.

Fallacies.—While no metal but arsenic yields the green precipitate, different organic substances give a green color, and, therefore, interfere with it. The arsenic precipitate, when dried and subjected to the *reduction test*, will give the metallic mirror. Dissolved in hydrochloric acid and subjected to Reinsch's test, the metal deposit will show on copper-foil.

Delicacy.—A green response has been obtained from $\frac{1}{10000}$ gr. of arsenic.

Ammonionitrate of Silver Test.—To prepare the reagent freshly dilute some ammonium hydroxid, as stated in the last test, and add to it a strong solution of silver nitrate until the precipitate of silver oxid formed ceases to dissolve. This reagent yields with solutions of arsenic trioxid a canary-yellow precipitate of silver arsenite, Ag_3AsO_3 (No. 3, Plate 2), which dissolves in ammonium hydroxid and in nitric acid, but not in sodium hydroxid. If dried and heated with flux, as in the reduction test, silver arsenite will be identified by the metallic mirror formed on the cooler part of the tube.

Fallacies.—Other chemicals, such as phosphoric acid, the alkaline iodids, and bromids, will give a like yellow precipitate.

Interferences.—The chlorids, hydrochloric acid, and organic matter decompose the reagent and interfere with this test.

Delicacy.—Minute yellow flakes are yielded by $\frac{1}{10000}$ gr.

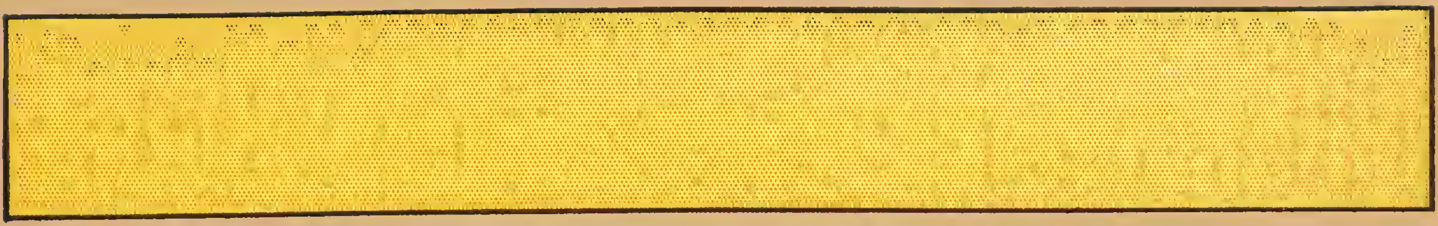
Bettendorff's Test.—A freshly made solution of stannous chlorid is added to the suspected material dissolved in strong hydrochloric acid. Having immersed a small piece of pure tinfoil, the mixture is heated; if arsenic be present, a brown color or a gray-brown precipitate of the metal is formed.

Delicacy.—A brown coloration is yielded by $\frac{1}{10000}$ gr. forming $\frac{1}{500000}$ of the hydrochloric-acid mixture.

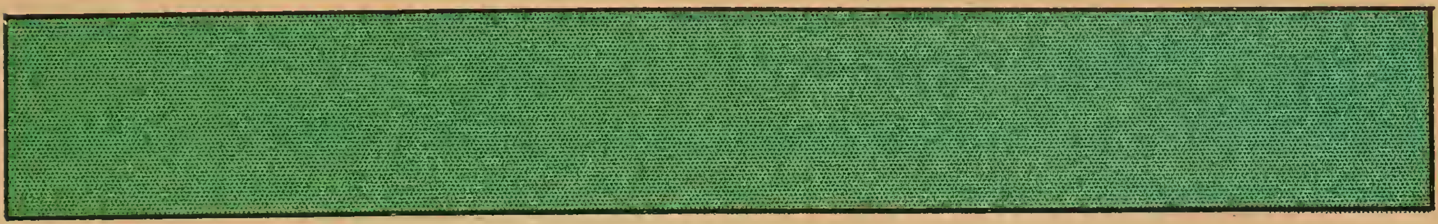
Tests for Arsenic in Complex Solutions.—To detect the arsenic in solutions with other matters the following tests are useful:

Hydrogen Sulphid and Hydrochloric Acid Test.—If the solution, acidified with hydrochloric acid and warmed, be sub-

PLATE 2.

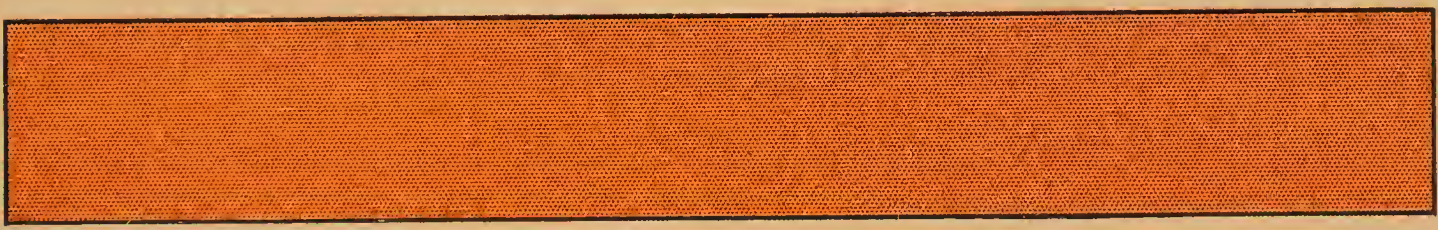


Arsenous sulphid produced in hydrogen sulphid and hydrochloric acid test for arsenic.



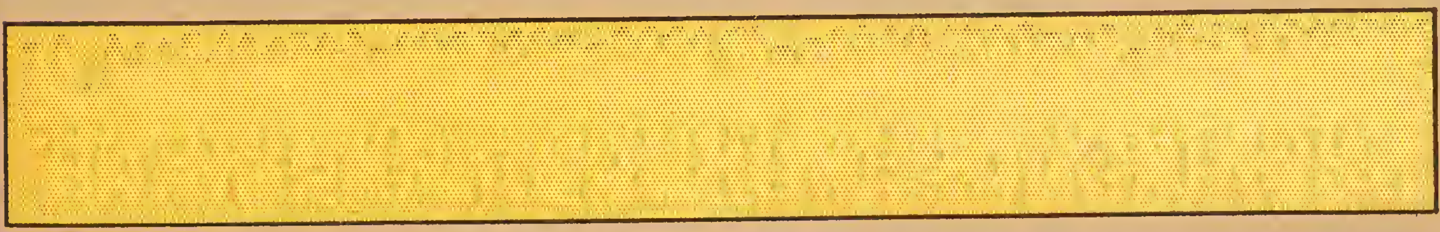
Cupric arsenite produced in ammonio-sulphate of copper test for arsenic.

Silver arsenite produced in ammonio-nitrate of silver test for arsenic.



Silver arsenate produced in arsenic solutions by treatment with silver nitrate.

Antimonous sulphid produced in hydrogen sulphid test for antimony.



Stannic sulphid produced in hydrogen sulphid test for stannic compounds.

jected to a current of well-washed hydrogen sulphid, bright-yellow arsenic sulphid, As_2S_3 (No. 1, Plate 2), will be thrown down.

$$2H_3AsO_3 + 3H_2S = 6H_2O + As_2S_3.$$

This deposit is insoluble in cold hydrochloric acid, but hot nitric acid decomposes it and forms solution of arsenic acid. It will dissolve in the alkalis and in ammonium sulphid.

Fallacies.—Yellow or orange precipitates may occur from cadmium, antimony, and tin, and the possible separation of sulphur from the hydrogen sulphid. To verify the nature of the precipitate it should be separated by filtration, dissolved in ammonia, evaporated to dryness, and subjected to the *reduction test* and the resubliming of the metallic mirror to octahedral crystals.

Delicacy.—A yellow turbidity, ending in a good deposit, has been obtained from $\frac{1}{10000}$ gr.

FIG. 63.—Apparatus for Gutzeit's test for arsenic.

Gutzeit's Test.—In a test-tube containing 1 c.c. of the suspected solution, either acid or neutral, put about 1 gm. of chemically pure zinc and 5 c.c. of a 6 per cent. dilution of sulphuric acid. In the upper part of the tube insert a plug of absorbent cotton moistened with lead acetate, and clasp over the mouth of the tube a cap made of three layers of filter-paper. Having wet only the upper layer with a drop of saturated solution of silver nitrate, set aside in a dark box for a time. Arsenic will cause on the paper a bright yellow spot, which darkens by separation of metallic silver when water is applied to it (Fig. 63).

$$AsH_3 + 6AgNO_3 + 3H_2O = 6HNO_3 + H_3AsO_3 + 6Ag.$$

The color made by antimony is at no time yellow, but is at once brown or black.

Reinsch's Test.—The purity of the materials for this test may be established by a blank experiment. A few slips of bright copper-foil should be put into pure water containing one-sixth part of hydrochloric acid, and then heat applied so as to boil for

five minutes. The copper remaining bright, the hydrochloric acid may be assumed to be pure; but every detail of this test and others must be paralleled by blank experiments before the analyst can be sure.[1] Having added one-sixth volume of hydrochloric acid to the solution to be tested, a strip of pure copper-foil is put into it and the whole boiled for a few minutes. If arsenic be present, as arsenous acid or arsenites, it is deposited as a dark film, purple to steel gray in color. From *arsenic* acid it is deposited only when the solutions are strong.

Fallacies.—A coating will be left on the copper by arsenic, antimony, mercury, bismuth, gold, and platinum; even prolonged boiling in hydrochloric acid may tarnish it. To verify the arsenic film the copper slip should be washed, dried with filter-paper, rolled into a cylinder, and inserted into a hard glass tube open at both ends, all by means of forceps, the finger not touching the foil. When the heat of a spirit lamp is applied, the metallic film sublimes and is deposited on the tube as a white ring of octahedral crystals of arsenic trioxid, which will dissolve in water and respond to ammonionitrate of silver and the other tests given above.

Beside arsenic there are two other metals, antimony and mercury, which make a sublimate under these conditions. Mercury makes a sublimate of shining globules; the antimony sublimate is generally amorphous, but may be in octahedral crystals.

To establish the arsenic nature of the sublimate the octahedral crystals must be well defined. In order to get the crystals deposited on a glass slide convenient for the use of $\frac{1}{4}$-in. objective, the following manipulations will be useful: Having obtained the arsenic stain on copper-foil, the foil is removed, washed, and dried without contact with the fingers, and cut into narrow strips. A subliming tube should be made of thin glass, diameter $\frac{1}{4}$ in., length $1\frac{3}{8}$ in., sealed at one end, and a lip turned back at the other open end, so that it will hold when hung in an opening made in a sheet of brass 4 in. $\times$ 2 in. The sheet of brass should be laid upon the ring of a retort stand, with the tube suspended, and then the tube warmed, so as to dry it. After cooling, the tube receives the strips, and a microscope slide, dried by heat, is placed upon it. The glass subliming-tube should then be heated, so as to permit the flame to play also on the bottom of the brass plate. A whitish sublimate will appear on the glass slide in a few seconds, but the heat should not be withdrawn until the white patch begins to clear up at the edges and has a diameter of $\frac{1}{4}$ in. The cold slide

[1] As ordinary copper itself may contain arsenic, it should be tested by first giving it a polished surface and then dropping a sample into a boiling mixture of equal parts of solution of chlorid of iron and pure strong hydrochloric acid. If impure, arsenic will show as a black coating.

examined by a $\frac{1}{4}$- or $\frac{1}{6}$-in. objective will show minute octahedra and tetrahedra, and modifications of these (see Fig. 64).

Interferences.—This test does not work properly if nitric acid, a chlorate, manganese dioxid, or other oxidizing agent is present. They cause the solution of the copper and prevent the formation of an arsenic coating. With this simple and delicate test it is possible for the physician to make an early diagnosis during life by examining the vomited matters or urine without any other preparation of the materials than digestion on the water-bath with 1 part of *pure* hydrochloric acid to 6 of the tested fluid. The copper slips can then be boiled in this fluid. Any marked darkening of the copper is significant usually of arsenic, antimony, or mercury.

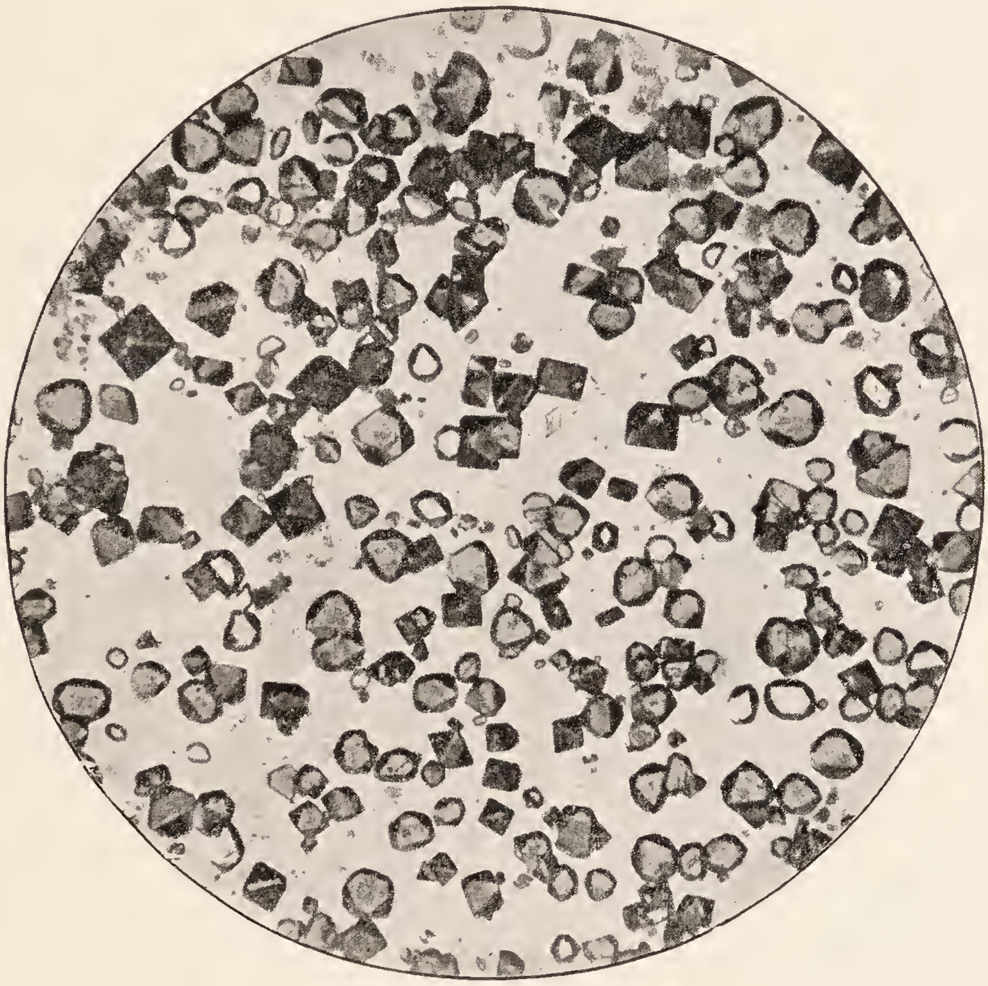


FIG. 64.—Sublimate of arsenic trioxid (magnified 340 diameters).

Delicacy.—With ordinary reduction tubes distinct octahedra form when only $\frac{1}{10000}$ gr. of arsenic is present; with great care, using very fine tubes, $\frac{1}{50000}$ gr. has been revealed.

Marsh's Test.—When hydrogen is generated in the presence of compounds of arsenic, they give up the arsenic, which, uniting with hydrogen, forms arsenic terhydrid, AsH_3 (p. 266). This is a gas which, by heat, yields the metallic arsenic for identification by tests already stated. In a flask arranged for generating hydrogen (Fig. 65), with air-tight connections, pure zinc is placed,[1]

[1] When pure zinc is used the evolution of hydrogen should be accelerated by a few drops of solution of platinum chlorid.

and pure cold dilute sulphuric acid (1 : 6) is added to it through the funnel-tube (*b*). The gas is first conducted through a drying tube containing calcium chlorid (*a*) between plugs of glass wool,

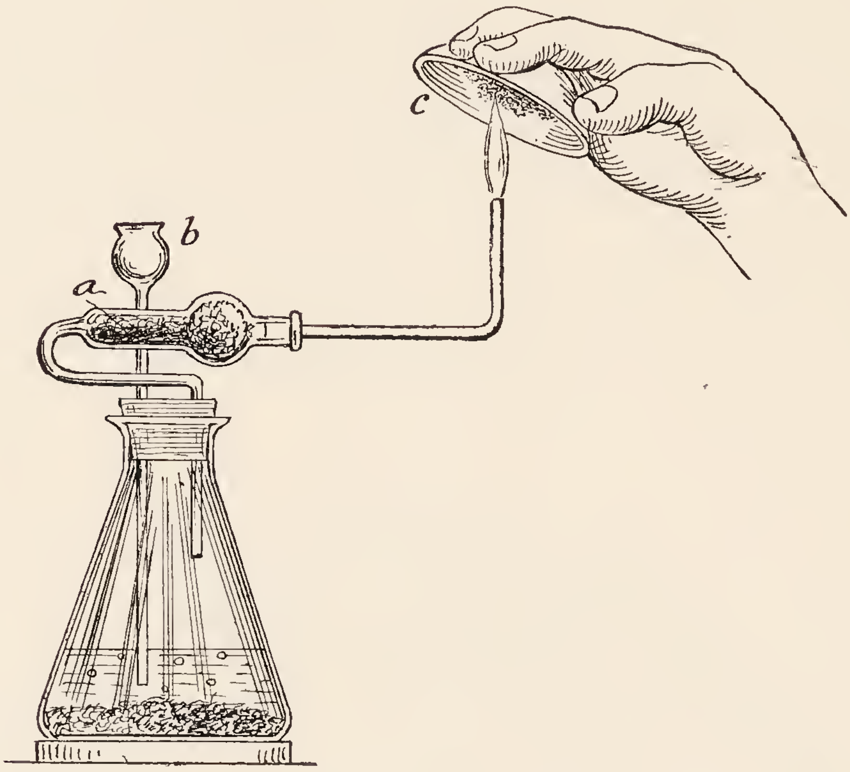


FIG. 65.—Marsh's apparatus for the detection of arsenic.

and then through an exit tube of hard glass, about 5 mm. ($\frac{3}{16}$ in.) internal diameter, and 25 to 50 cm. (10–20 in.) long, which is turned up at the end and drawn out at the tip to make a jet. After waiting a few minutes for the air in the apparatus to escape a Bunsen flame is applied in the course of the exit tube, which is heated to a low red heat, and if no stain appears on the glass after fifteen minutes, the chemicals may be considered pure. The gas jet should be ignited, and if arsenic fluid is now poured in by the funnel tube in small portions, the pale hydrogen jet becomes more luminous and livid in color. If organic matter should cause much frothing, a small quantity of alcohol may be introduced by the funnel tube.

Marsh's Original Method.—To prove the presence of arsenic in the gas Marsh proposed to condense the free metal on cold porcelain held in the flame (Fig. 65, *c*). It is like a spot of soot: black or seal brown. Many spots can be obtained upon evaporating dishes or crucible lids and tested later by different reagents to distinguish them from the antimony stains which they resemble closely.

Berzelius' Modification.—The most delicate, reliable, and, indeed, necessary method for detecting the arsenic with the Marsh apparatus for forensic purposes is to heat the gas while passing through the long exit-tube by applying to it one or more burners

with chimneys to confine the heat. For the best results the tube may be constricted at points just beyond the part heated, and the constricted part kept cold by a wet muslin strip (Fig. 66, *h*).

If a dull red heat is maintained for an hour, all the arsenic will be separated from the mixture and collected as a mirror-like ring inside the tube between *k* and the strip of wet muslin. The discrimination tests given below can be used to confirm the arsenic nature of this metallic ring, as well as for the spots on porcelain.

Fallacies.—Antimony is deposited under the same conditions as arsenic, and in a form closely resembling it, whether in the spots on porcelain or the mirror-like ring in the heated tube, but the

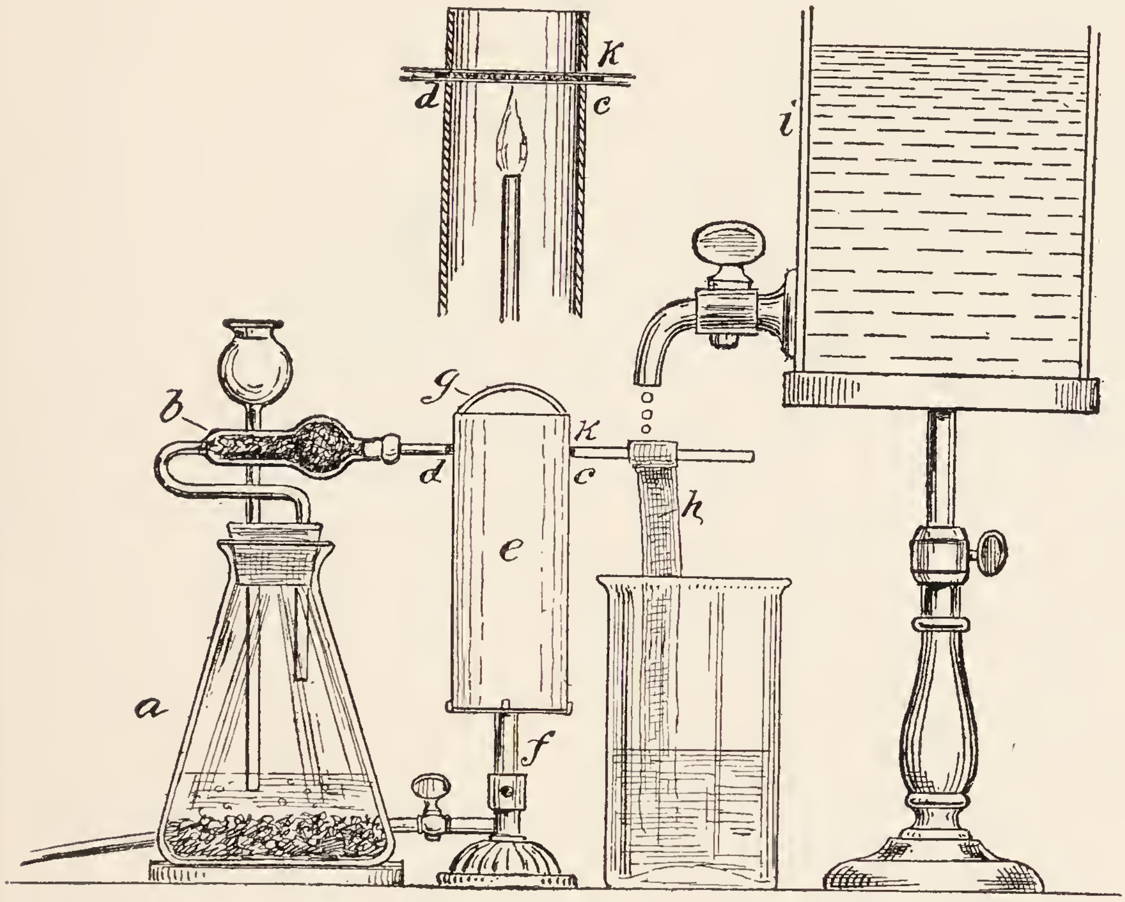


Fig. 66.—Modification of Marsh's apparatus to secure the most delicate results: *a*, Generating bottle; *b*, calcium chlorid tube; *c*, point where hard glass tube narrows from $\frac{1}{4}$ to $\frac{1}{8}$ in., a small plug of asbestos inside; *d*, a small plug of asbestos; between *c* and *d* a mixture of dry sodium carbonate and charcoal; *e*, a fire-clay chimney $1\frac{3}{4}$ in. in diameter, with a thin bridge of fire-clay to support the tube between *c* and *d*; *h*, a strip of muslin $\frac{1}{4}$ in. wide wrapped around the tube and tied.

arsenic mirror is at a little distance beyond the flame and brownish, shading to black (Fig. 67, *a*), while the antimony is close to the flame, sometimes on both sides of it, and tin-like in luster.

The arsenic stains are soluble in warm solution of *calx chlorinata* or *liquor sodæ chlorinatæ*, while the antimony is insoluble, or only very slowly and sparingly soluble. Dissolved by heating gently with a few drops of a solution of ammonium molybdate in nitric acid, the arsenic gives a yellow precipitate, whereas antimony forms none. Another deposit dissolved in nitric acid and dried by cautiously heating leaves a whitish spot which, if arsenic,

turns red when touched by a drop of strong solution of silver nitrate (Fig. 67, *c*); if antimony, there is no change of color (Fig. 67, *d*). Another deposit, if arsenic, dissolves in ammonium sulphid and on evaporation leaves a yellow stain soluble in ammonia, but insoluble in hydrochloric acid. The residue of antimony sulphid would be orange-red, insoluble in ammonia, but soluble in strong hydrochloric acid.

The extraordinary sensitiveness of most of the tests for arsenic requires that the analyst should be very careful that the apparatus is clean and the chemicals are of ascertained purity. In medico-legal analysis it is well to carry on simultaneously a parallel blank

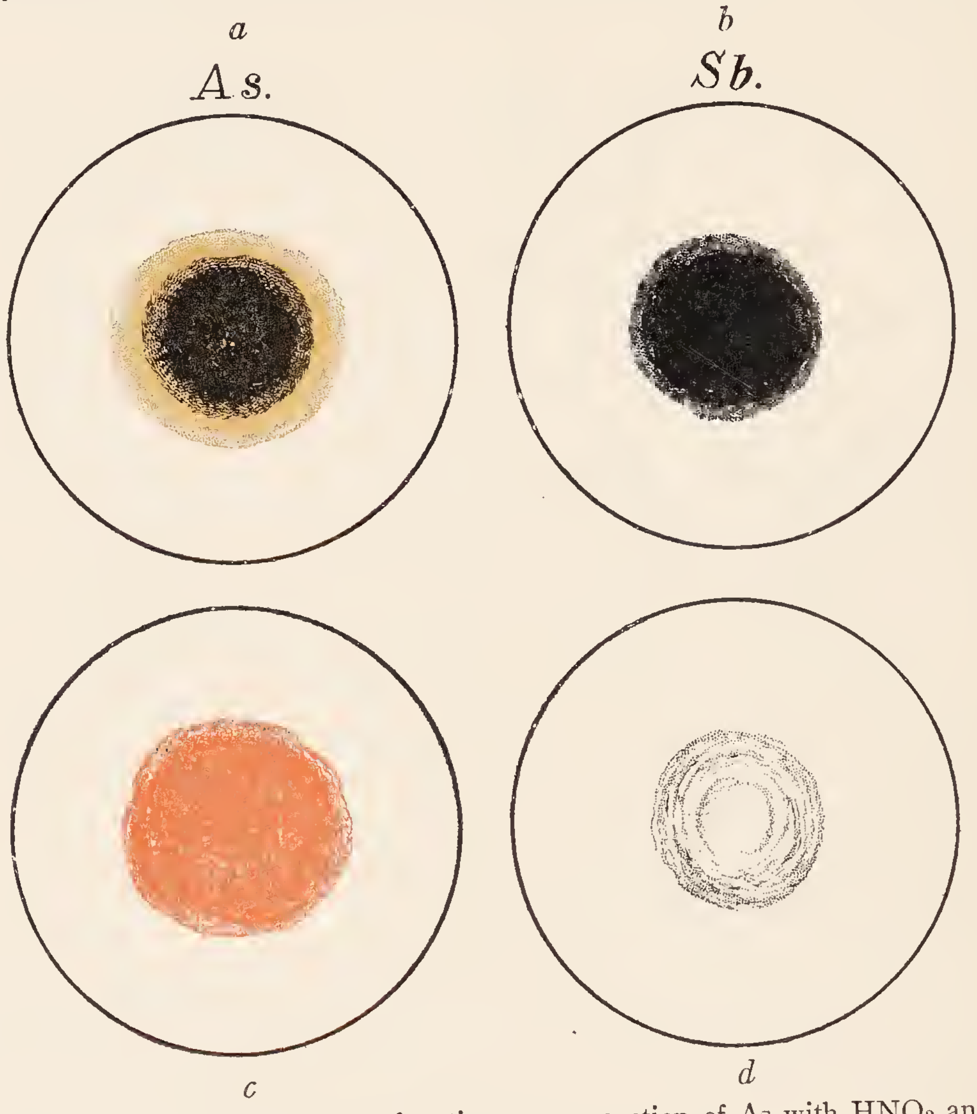


FIG. 67.—*a*, Mirror of arsenic; *b*, mirror of antimony; *c*, reaction of As with HNO_3 and $AgNO_3$; *d*, reaction of Sb with HNO_3 and $AgNO_3$.

examination, similar in every respect but that of containing the suspected matters. Traces of arsenic have been found in zinc, copper, sulphuric acid, hydrochloric acid, even in filter-paper, and in common illuminating gas. Glass vessels that have been cleaned with shot may have enough left on them to lead to a false conclusion.

Interferences.—The perfection of Marsh's test is impaired if chlorids, hydrochloric acid, nitrous compounds, or nitric acid be present. If salts of silver or mercury be present, they may decompose the arsenic terhydrid in the flask as soon as it is generated.

Delicacy.—To operate this test even on a small scale requires at least 100 gr. of the liquid. The least amount that would yield a satisfactory spot on porcelain is about $\frac{1}{5000}$ gr. of arsenic trioxid. When the gas is not ignited, but heated in the exit tube so as to get all the free metal at one point, we get a degree of sensitiveness beyond that reached by any other test known to chemistry. By this Berzelius' modification of Marsh's test a characteristic deposit on the glass can be obtained from $\frac{1}{50000}$ gr. dissolved in 100 gr. of liquid.

Fleitmann's Test.—When zinc or aluminum is heated with excess of potassium hydroxid or sodium hydroxid in a mixture containing arsenic trioxid or trisulphid, the gas arsenic terhydrid is evolved:

$$Zn \quad + \quad 2KOH \quad = \quad K_2ZnO_2 \quad + \quad H_2.$$

The apparatus required is a generating flask with a delivery tube dipping into a 4-per cent. solution of silver nitrate. It is sometimes more convenient to use a test-tube covered with filter-paper wet with silver nitrate, as in Gutzeit's test (Fig. 63). The suspected liquid, made strongly alkaline with pure sodium or potassium hydroxid, is put in the flask or the test-tube with a few pieces of sheet aluminum or pure zinc and gently heated. The arsenic terhydrid reduces the silver as a black precipitate, leaving arsenic trioxid and nitric acid in solution. If the test-tube is used, a black spot appears on the paper cover. By means of this test we can detect arsenic in the presence of antimony, as antimony terhydrid is not evolved by it. It will not detect arsenic as arsenic acid, and as it forms solid hydrid in the flask, holding back one-fifth of the arsenic present, it is not available for quantitative purposes. It is liable to a fallacy from the fact that free hydrogen after some time and phosphin both reduce the silver nitrate; hence, the presence of arsenic trioxid in the silver solution must be proved by other tests.

Detection in Gastric Contents and Viscera.—The vomited matter should be spread in a thin layer on a large dish and carefully searched for grains of white arsenic, Paris green, or yellow sulphid. For casual or preliminary examination the suspected material may be treated as suggested above by Reinsch's test. The presence of the smallest amount is significant, as arsenic is not a constituent of the body in general, nor should it be present in the food. If any compound of arsenic should be found free in the gastric contents, or if it should be obtained by testing, a specimen of it must be carefully marked and set aside to show in court.

When it is desired to make a *quantitative* estimate, it is necessary to destroy the organic matter. This may be done by mincing the tissue into fine shreds, bruising these in a mortar, heating

over a water-bath in pure dilute hydrochloric acid (best made in the laboratory), and adding, from time to time, small portions of potassium chlorate until the solids are completely dissolved in a clear yellow fluid and continuing a gentle heat until the odor of chlorin disappears. This fluid is treated with solution of sulphur dioxid to reduce the arsenic compound to the arsenous form, then concentrated on a water-bath and filtered. A slow stream of hydrogen sulphid passed through the filtrate will precipitate the arsenic as arsenous sulphid with other matter. The precipitate is collected on a filter, thoroughly washed, and treated with ammonia-water, which dissolves out the arsenous sulphid, leaving various impurities behind. The filtered solution is evaporated to dryness in a porcelain dish, the residue warmed with strong nitric acid until completely oxidized, and solution of sodium hydroxid added in slight excess. The mixture is evaporated to dryness, the residue moistened with pure sulphuric acid, and heated cautiously on a sand-bath until fumes cease to escape. The carbonaceous product is boiled out with acidulated water and the solution filtered. The filtrate should be colorless, and, if the process has been properly executed, contains all the arsenic free from organic matter. As the arsenic generally exists in the solution wholly or in part as arsenic acid, sulphurous acid should be added to reduce it to the arsenous condition, and the mixture gently heated until all excess of the sulphur dioxid has been expelled. A definite part of this solution may be reserved for determining the amount of arsenic by precipitation with hydrogen sulphid, as described below, while the remainder may be subjected to Reinsch's, Marsh's, and other tests to establish fully its arsenic character.

Nitric acid, assisted by sulphuric acid, is sometimes used to destroy the organic matter and oxidize the arsenic into arsenic acid. In such a case the arsenic acid can be readily extracted by boiling water, and the solution filtered and evaporated to dryness. Marsh's test can be applied to the solution, and metallic arsenic will appear as a mirror on the tube or on cold porcelain.

In order to *estimate* the arsenic the total quantity of fluid obtained, as above, from any organ, such as the liver, should be divided into equal parts, and one or more of these parts used to get a deposit of metallic arsenic in the heated tube by the Marsh-Berzelius method. The section of coated tube is cut off and weighed, and then washed free from arsenic with nitric acid or solution of sodium hypochlorite and weighed again. The difference represents the amount of arsenic in the portion of the material used. The brown deposits, which are more or less transparent, consist of the suboxid, As_2O, and hydrid, AsH_3; hence these quantitative results can never be absolutely accurate. Another method

of *estimating* is by converting the arsenic into sulphid. A measured fraction of the dissolved materials, acidified with hydrochloric acid, is treated with a stream of pure, washed hydrogen sulphid gas. The yellow precipitate is collected on a filter, thoroughly washed, and then dissolved in ammonium hydroxid. By evaporating the solution thus obtained on a water-bath, the ammonia is removed and the dried sulphid, after treatment with carbon disulphid to dissolve out any free sulphur that may be present, is weighed, and the calculation made on the basis that 100 parts of the sulphid contain 60.98 of elementary arsenic. As arsenic acid and the arsenates are precipitated very slowly by hydrogen sulphid, they will require other treatment (see p. 287).

When the amount of organic matter present is small, as in the *urine*, the test for arsenic can be got at by a more direct method. Concentrated sulphuric acid containing $\frac{1}{30}$ its volume of nitric acid is added to the residue of urine, which has been evaporated to dryness over a water-bath, and the mixture is heated until dense white fumes are given off. The charred materials are extracted with boiling water, the solution concentrated over a water-bath, and introduced at once into the Marsh apparatus.

Detection in Wall-paper.—When there is reason to think that the amount of arsenic is considerable, resort may be had to Reinsch's test. Five square inches of the paper cut finely are put in a dish with dilute hydrochloric acid, and heated on a water-bath for fifteen minutes. The solution is then decanted into a test-tube, a piece of polished copper-foil added, and then boiled for ten minutes. The arsenic coating on the copper can be verified by the confirmatory tests given on p. 277.

When the amount present is so small as to give a doubtful result to Reinsch's test, it may still be revealed by the Marsh-Berzelius method. The arsenic is dissolved from the paper as stated above, and the acid solution poured into the Marsh apparatus (Fig. 66). The blackness of the arsenic mirror formed in the glass tube, when compared with a series of standard arsenic mirrors, will give an approximation to the quantity.

Distribution of Absorbed Arsenic.—Besides that which may be found in the contents of the stomach and intestines, a variable proportion of arsenic is absorbed, and by the blood and other fluids is distributed to different organs and tissues. This latter part has certainly had a poisonous effect, whatever may be said of that found unabsorbed. Even when none has been found in the contents or even the structure of the stomach and the intestines, the liver, kidneys, spleen, and heart have rendered up their store to the analyst. The muscular and bony tissues and the brain are also places for the deposit of absorbed arsenic.

It not infrequently happens that the arsenic is taken in a very soluble form, and, the patient surviving for two weeks or even less, no poison can be detected in the viscera usually examined. This is due to the activity of the circulation in the soft tissues and the readiness with which the poison is eliminated. Under such circumstances, several observers have discovered the poison still present in the cancellated structure of the bones and in the nails and hair. Arsenic has been detected in the urine ninety-three days after a single large dose had been administered, causing acute symptoms and having a sequel of paralysis.

Failure to Detect.—Instances are known of undoubted poisoning in which no trace of the arsenic has been found in the parts usually examined. The eliminating organs had time before death to expel the unnatural substance.

Normal Arsenic.—Gautier found arsenic in the tissues of the thyroid and thymus glands, the skin, and the brain, chiefly in the form of nuclein iodid. Later he reported it constantly present in the fresh thyroid of man. A trace was found in the hair of a man and also of a woman, neither of whom had ever taken arsenic. Some was detected in the thymus of a lamb. Traces were discovered in the mammæ of a cow and in two quarts of her milk. Fresh bone furnished a trace. The brains of two stillborn children showed its presence, but it was absent in a third. He failed to find arsenic in the presumably healthy tissue of liver, kidney, spleen, muscles, testicles, pituitary gland, mucous membrane, cellular tissue, lymphatics, salivary glands, suprarenal capsules, bone-marrow, uterus, ovaries, blood, urine, and feces. Upon examining various foods he found it absent from bread, fish, eggs, and meats, excepting the tissues named above—viz., milk, thymus, thyroid, skin, and brain. It was present in the following vegetables: cereals, turnips, cabbages, and potatoes. In case arsenic should be found in the tissues named above as normally free from it, the inference would be that arsenic had been taken as a medicine or criminally.

Measurable quantities of arsenic have been found in 1 gm. of the hair of several persons having arsenic neuritis, and a trace has been detected in the same amount of hair from healthy subjects.

Hödlmoser, W. Thomson, and also Wieser reach a conclusion opposed to that of Gautier. Their researches showed that arsenic is not a normal constituent of the human body, though it is often accidentally present in animal and human tissues. Not even a trace of arsenic was found in the liver and pancreas in 18 cases examined by Gautier's method, nor in 15 other cases in which the same viscera were examined by another process esteemed

more delicate. In repeating the experiments of Gautier, referred to on different tissues, they always obtained negative results.

Arsenic Pentoxid (As_2O_5) (*Arsenic Acid*).—This commonly occurs in white, vitreous, deliquescent masses, but may be obtained as rhombic crystals. The pentoxid deliquesces in the air and changes to the true arsenic acid, $As_2O_5 + 3H_2O = 2H_3AsO_4$. This acid is produced immediately by oxidizing arsenic trioxid, when it is heated with nitric acid in the presence of water, $As_2O_3 + O_2 + 3H_2O = 2H_3AsO_4$. Like phosphoric acid (page 189), it is tribasic and forms three series of salts, according to the number of hydrogen atoms replaced. It also loses water in stages forming pyro- ($H_4As_2O_7$) and meta- ($HAsO_3$) acids like the corresponding forms of phosphoric acid. The ortho- or common arsenic acid is a colorless, syrupy liquid with a metallic taste. Like arsenic trioxid, it is an irritant poison. The free acid is not used in medicine, but some of its salts are. It is much used in the manufacture of dyes, although recently other oxidizers have supplanted it to a considerable degree. It responds to the same tests as arsenic trioxid, but has a peculiar reaction with silver nitrate, forming a brick-red precipitate (Plate 2, No. 4). It will respond to Marsh's test, but it is precipitated very slowly by hydrogen sulphid. If there be reason to think that either arsenic acid or any arsenate is present in the tested fluid, it should be reduced to arsenous acid by a current of sulphur dioxid and the latter removed by passing carbon dioxid before the hydrogen sulphid is added to it. A solution of sodium arsenate, 4 lb. to 1 gal., is commonly injected by undertakers through the nostrils into the stomach and into the thoracic cavity in order to arrest decay in warm weather. Sometimes cloths are wet with it and wrapped about the corpse to accomplish the same end.

Presence of Arsenic in Various Substances.—Medicinal Preparations.—The arseni trioxidum of the U. S. P. (white arsenic, As_2O_3) is present to the amount of 1 per cent. in each of the following preparations: *liquor acidi arsenosi* in 5 per cent. dilute hydrochloric acid; *liquor potasii arsenitis* (Fowler's solution); *liquor sodii arsenitis* (Harle's solution). Donovan's solution, or *liquor arseni et hydrargyri iodidi*, contains 1 per cent. each of arsenous iodid, AsI_3, and mercuric iodid, HgI_2, while Pearson's, or *liquor sodii arsenatis*, contains 1 per cent. of exsiccated sodium arsenate, Na_2HAsO_4, $7H_2O$. *Sodii arsenas* occurs as colorless, odorless prisms, soluble in water. *Sodii arsenas exsiccatus* is an amorphous white powder, permanent, very soluble and double the strength of the hydrous salt just mentioned. *Arseni iodidum* occurs as an orange-red crystalline powder, water-soluble with slight decomposition. *Cacodyl*, $2As(CH_3)_2$ (*dimethylarsin*), is a volatile, colorless liquid with garlic odor and poisonous.

Cacodylic acid, $As(CH_3)_2O_2H$, is a white crystalline substance, soluble, odorless, and comparatively non-poisonous, though it contains 54 per cent. of elementary arsenic. In overdoses it causes the same symptoms as arsenous acid. *Sodium cacodylate*, or *sodium dimethylarsenate*, $As(CH_3)_2O_2Na$, a white soluble powder, while generally well borne in large doses (of 1 to 3 gr.), may undergo changes when given by the stomach or the rectum and have toxic effects. It contains arsenic in a complex organic group and very high proportion, but usually liberates the active arsenic ion in the body slowly and safely. It is eliminated in the urine as arsenates. The same can be said of *atoxyl*, $C_6H_4(NH_2)$ (AsO. OH.ONa) (sodium aminophenyl arsenate), which is a white odorless powder, water-soluble, containing 26 per cent. of arsenic. Given like these hypodermically is the sodium salt of *arsen-phenol-amin*, "salvarsan," $2(As.C_6H_3.OH.NH_2.HCl)$. It is a yellow powder kept in sealed tubes. It forms in water an acid solution. For intramuscular injections a suspension of the free base is made by cautious addition of sodium hydroxid to neutralization. This is used to destroy the microbes of syphilis and other diseases by a few massive doses; a dose above 0.6 gm. would be risky and 10.5 gm. might prove fatal. To obviate the difficulties of preparation, "*neosalvarsan*" is sold. This is a combination of salvarsan with sodium-formaldehyd sulphoxylate. It makes a neutral solution in water convenient for intravenous doses of 0.75 gm. There is no essential difference in toxic or therapeutic effects between salvarsan and neosalvarsan. Fatalities with arsenical symptoms have occurred after taking either of them. It sometimes happens that the biochemical agencies of the body split off the arsenic from the complex groups in a toxic form and in fatal amounts from doses ordinarily deemed perfectly safe. An *arsenic* paste has been applied to tumors by cancer quacks so unskilfully as to produce systemic poisoning by absorption. The manufacturers of gelatin-coated and sugar-coated pills sell large quantities of tonic pills containing arsenic as a constituent. It is often a contaminant of commercial glycerin and of subnitrate of bismuth. In 1 out of 8 samples of bismuth subnitrate examined arsenic was found; it was present to the amount of 0.33 per cent. of the element. In this preparation it probably exists as bismuth arsenate, a form not readily absorbed because of its insolubility.

In Preservatives and Cleaners.—In order to keep wheat for planting it has been treated with an arsenic solution which does not alter its appearance or taste. Samples so treated have caused accidental poisoning. A mixture of white arsenic, tar, and soft soap is sometimes used as a "sheep dip" to destroy the parasites in wool. The sheep-washers have experienced poisonous effects from handling it and from drinking water from a vessel that once contained it. Taxidermists make use of an arsenic soap and an

arsenic powder to preserve skins. The workmen have suffered, and it is stated that poisonous symptoms can be traced to the arsenic emanating from stuffed specimens kept in sleeping-rooms. Wholesale poisoning has followed the introduction into a boiler of a "cleaner" made from arsenic and sodium bicarbonate. A similar solution has been used as a "soft injection" or preservative of bodies for dissection. Dissectors handling the bodies are likely to have a local irritation about the finger-nails.

In Anilin Dyes.—Arsenic acid or arsenic pentoxid is frequently used as an oxidizer by the color-men in the preparation of anilin red and other pigments. It is not a necessary ingredient of the pigment, and at this time is not so often found in it as formerly. The expense of washing out this residuum still sometimes deters the manufacturers, and the dye may come into the market with enough arsenic in it to give irritant properties to stockings, gloves, and cretonne bed-trimmings reddened with it. This impure anilin red has been used to color strawberry and raspberry syrups.

In the Air.—In the chemical laboratories 8 deaths have occurred from the accidental inhalation of the vapor of arsenureted hydrogen escaped from the Marsh apparatus. It has destroyed life in quantities so small as not to impart a garlicky odor to the air. Traces of this poison have been found in common illuminating gas. By some writers this is the form supposed to be taken by the arsenic emanations of wall-paper, though other authorities suppose the emanation to be an organic compound, such as cacodyl oxid. In the extraction of gold and silver from certain ores, the cleaning of iron for tinning and of brass for bronzing, acids are used which liberate hydrogen. This nascent hydrogen unites with arsenic impurities in the ores or the metal, if any be present, and thus poisons the air breathed by the workmen. Arsenic poisoning has been caused by the fumes from a coke stove and also by the smoke from smelting works.

In Beer.—The glucose used in brewing sometimes contains arsenic. It is left in the glucose by the sulphuric acid employed in the conversion from starch when the acid is obtained from arsenic iron pyrites. Extensive poisoning occurred in the Midland counties of England attributed to arsenic in beer, and extended through six months. The most frequent characteristic symptoms were catarrh, puffiness of the eyelids, irregular pigmentation of the skin, herpes, and other eruptions, local numbness, tingling, and pain, with final paralysis. Arsenic was detected in the urine and in the hair. The amount of arsenic found in different samples of beer varied from $\frac{1}{100}$ to $\frac{3}{10}$ gr. to the gallon.

In the Household.—Many cases of poisoning, accidental or otherwise, have been traced to things in common domestic use.

"Fly-papers" for killing flies are sheets of paper saturated with sweet solutions or pastes of arsenic. Single sheets have been examined which contained 10 gr. of arsenic trioxid available for the poisoner. "Fly-powders" have been made by pulverizing the mineral arsenid of cobalt. "Buffalo Carpet-moth Annihilator," intended to be dusted over the carpet, is a powder containing arsenic. White arsenic is often mixed with a dough of flour or cornmeal and distributed in cellars and pantries to kill mice. The most extensively used domestic vermin-killer is "Rough on Rats," a mixture of white arsenic and barium carbonate. It is a gray powder procurable in every drugstore without restraint or legal registration. In this country a large number of suicides and some homicides have been caused by this agent. Among the means for wilful death it appears to be our national favorite. It is cheap, knowledge of its deadly properties is common, and there is every facility for purchasing it under the excuse of killing vermin. It is much to be desired that our State and municipal legislation relative to the sale of arsenic commodities should be shaped after the pattern of other civilized countries. Some provision should be made in the laws of every State which would require apothecaries to keep an arsenic book for recording sales of this poison, and which would forbid the sale of arsenic in any shape for the purpose of destroying vermin or for the embalming of dead bodies.

To overcome the gypsy moth and other leaf-eating insects the white precipitate of lead arsenate, $Pb_3 2AsO_4$, is sprayed over the foliage of plants. "Arsenic balls" are given by grooms to improve the coats of horses. Some kinds of white enamel-ware and some glass contain arsenic. It has been found in the silk lining of coat-sleeves, the glazed leather lining of hats, the brown paper lining of carpets, and the black cambric lining of furniture. It is sometimes present on the glazed paper and cardboard used for boxes, playing-cards, note-paper, and fancy wrappers for candy lozenges. At one time arsenic pigments were extensively used for coloring wall-hangings, lambrequins, cretonnes, chintzes, tarlatans, and artificial flowers and leaves. It has been alleged that numerous cases of slow poisoning have been traced to the arsenic from these sources pervading the atmosphere of dwellings. In making a diagnosis reliance has been placed upon the discovery of traces of arsenic in the urine of patients. It has been found there with surprising frequency.

Traces of arsenic, copper, and mercury have been detected in the urine of numerous healthy individuals examined. These substances are not totally eliminated by the organism, and in time the accumulated amounts from domestic sources might have an important bearing in certain medicolegal cases.

A volatile arsenic compound, probably a methyl arsin, CH_3As_2H, is produced by certain common moulds growing in contact with arsenicated substances such as might be used in wall-papers.

In the present state of knowledge no wall-paper containing as much as 0.1 gr. of arsenic in a square yard can be considered as harmless.

In Common Pigments.—Both accidental and intentional poisoning occur from the use of the pigments described below:

Scheele's green (copper arsenite, $CuHAsO_3$) contains 52.8 per cent. of arsenous acid. A bright green paint is made by mixing this with the basis of oil-paints and of water-colors. Although the public is warned as to the deadly character of this pigment it is still much used for giving color to wax tapers, toys, book-covers, artificial flowers, oilcloth, calicoes, cretonnes, and tarlatan. An equivalent green color and one much less injurious can be made by mixing Prussian blue and chrome yellow.

Paris green (copper aceto-arsenite, Schweinfurth green) is a color made by mixing the acetate of copper with the arsenite. It contains over 50 per cent. of arsenic. There is an enormous consumption of this compound as an application to the potato plant to rid it of the Colorado beetle. Used on the tops, this does not affect the edible tuber under ground. The same practice upon the tobacco-plant is far from innocent, as the leaves here are the parts to be used. It is often taken by suicides, but its color usually prevents its criminal use, though occasionally accidental death has been caused by it.

Arsenic trisulphid (As_2S_3) (*orpiment, King's yellow*), containing 61 per cent. of arsenic, is a yellow powder precipitated from acid solutions of arsenic by hydrogen sulphid. By mistake it has sometimes been substituted for the harmless vegetable pigment, turmeric. The action is similar to that of white arsenic. Arsenic trisulphid is insoluble in water and acids, but soluble in the alkalis and their carbonates, and in soluble sulphids and hydrosulphids. When precipitated with other metals from acid solution by hydrogen sulphid, it can be separated from all other sulphids by means of its solubility in ammonium carbonate.

When a dilute solution of arsenous acid is treated with hydrogen sulphid, the solution turns yellow without precipitation. Its effects on transmitted light show that the arsenic trisulphid is not in solution, but is suspended in particles too small to be stopped by filter-paper or to be seen with a microscope. If small quantities of solutions of electrolytes such as acids and ordinary neutral salts are added, the sulphid separates in visible flakes. These properties are characteristic of the class of *colloidal solutions*.

Arsenic disulphid, As_2S_2, *realgar*, occurs in ruby-red crystals containing 70 per cent of arsenic. It can be made by fusing sulphur and arsenic together. It dissolves in alkalis and their carbonates.

Arsenic in the Soil.—Some soils naturally contain arsenic in an insoluble iron compound. Headden has found that other virgin soils yield traces to water as a solvent.

After the use of superphosphate as manure, arsenic may be imparted by the impure sulphuric acid used in its manufacture. Paris green, sprinkled to kill bugs on the plants of potato, cabbage, or beets, adds some to the soil. Lead arsenate and calcium arsenite as insecticides sprayed on orchard trees furnish a soluble fraction to the ground and the rootlets absorb it. In a number of years the soil of sprayed orchards is 10 to 28 times stronger in arsenic than was the virgin soil. Potatoes, turnips, beets, oats, alfalfa, apples, pears, and the flesh of cattle grown on such a soil have all given signs of arsenic.

Persons eating freely of apples from sprayed trees secrete urine showing arsenic. From such food-plants and meats the human body may get the trace often found postmortem, even if the arsenic-enriched soil does not supply it to the corpse after burial. In cities it is the general custom for undertakers to embalm corpses by pumping a solution of sodium arsenate through the nostrils into the stomach, trusting to the high diffusibility of that salt to carry it throughout the body. Experiments show that in twelve days the arsenic may permeate the entire body, reaching the brain. It is probable that this same compound would eventually pervade the soil of the cemetery contiguous to a buried corpse. Ekeley's[1] research showed marked traces of arsenic very near a corpse buried in an arsenic-free cemetery.

ANTIMONY (*Stibium*)

Symbol, Sb. Atomic weight, 120.2

Antimony is a brilliant gray-white solid with a crystalline, metallic fracture, tasteless and odorless. When heated it volatilizes; at a higher temperature it burns to white fumes of antimony trioxid, Sb_2O_3. It is used as an alloy in type metal, Britannia metal, brass, and bell metal. Though the metal may not be poisonous, its salts are.

While poisoning from antimony was quite common in the Middle Ages, in our times it is comparatively rare. Cases have been reported from inhalation, probably of the trioxid, in certain industries. Lozenges containing the same preparation were the cause of poisoning in another case. In modern toxicology but two forms figure to any extent, the trichlorid and tartar emetic.

Sulphurated antimony (*Kermes mineral*), a mixture of Sb_2S_3 and Sb_2O_3, is employed in vulcanizing rubber. The India rubber connections of the Marsh apparatus might thus contribute a trace of antimony, unless care be taken to avoid the use of fittings made with this preparation. It is a constituent of the medical preparation, *Plummer's pill.*

[1] J. B. Ekeley, "Jour. Am. Chir. Soc.," 1913, xxxv., p. 483; quoted in "Jour. Am. Med. Assoc.," editorial, May 31, 1913.

Antimony trioxid, Sb_2O_3, occurs as a white powder of basic properties, although, because it corresponds to As_2O_3, it is sometimes erroneously called *antimonious acid.* It dissolves in alkalies; hence, undergoes some change and possibly forms an anion, as in the formula $H^{\bullet}$, (SbO_2); thus, sodium meta-antimoniate is $NaSbO_2$. Dose: 1 to 3 gr. (0.06–0.2 gm.). It is a component of *James' powder*, which contains calcium phosphate with antimony trioxid.

Antimony terhydrid (SbH_3) (*antimoniureted hydrogen*) is a colorless, odorless gas, corresponding to arsenic terhydrid. It is given off when zinc and sulphuric acid react in the presence of an antimony salt. It differs from arsenic terhydrid in having no garlicky odor and in being less poisonous.

Antimony trichlorid ($SbCl_3$) (*butter of antimony*) occurs as a soft solid. A strong solution of the chlorid in hydrochloric acid is employed in the arts as a *bronzing* liquid and in farriery. It crystallizes white and transparent. Added to water, a whitish precipitate falls, of *antimonyl chlorid*, SbOCl.

The records of 8 cases of poisoning show that in the 4 fatal ones the dose was 2 oz., while 2 that recovered took 1 oz. each. A woman of forty years died in less than two hours; in her stomach were found 8 gr. of antimony and 0.1 gr. of arsenic.

Tartar Emetic ($KSbOC_4H_4O_6$) (*Tartarated Antimony, Stibiated Tartar, Antimonii et Potassii Tartras*).—This is a white crystalline powder with an acrid, disagreeable, metallic taste. It is made by the action of a boiling solution of cream of tartar upon antimony trioxid. Dose: $\frac{1}{8}$ to 3 gr. (0.008–0.2 gm.). It may be regarded as acid tartrate of potassium, $KHC_4H_4O_6$, the hydrogen of which is replaced by the radical antimonyl SbO. It has been dispensed by mistake for cream of tartar and for tartaric acid. It is soluble in cold water, more readily in hot water, but insoluble in alcohol. Wine is used as a vehicle in *vinum antimonii* (0.4 per cent. tartar emetic), the water of the wine acting as a solvent and the alcohol checking the formation of the moulds, to which a simple aqueous solution is liable. It is present in *syrupus scillæ compositus* ("Hive Syrup"), dose: 15 to 60 ♏ (1–3 c.c.), and in *unguentum antimonii.*

Symptoms.—There is a close resemblance between the symptoms caused by antimony and those produced by arsenic. While it occasionally happens that large doses (200 gr. of tartar emetic) do not cause vomiting, as a rule, nausea, retching, and vomiting come on within half an hour and continue as conspicuous features of the clinical picture, which may be sketched as follows: In a few seconds there is an acrid and metallic taste, followed by a sense of constriction in the throat and pain in the stomach; frequent and profuse vomiting, sometimes of bloody material; diarrhea with

watery discharges, sometimes involuntary, sometimes attended with tenesmus; fainting attacks and depression, characterized by a feeble and frequent pulse and profuse sweating; spasmodic contraction of the arms, fingers, and legs. In very grave cases the urine may be wholly suppressed, the temperature subnormal, the skin cyanotic, and death be ushered in by delirium, convulsions, and coma. There are exceptional cases in which no vomiting occurs for an hour, and others in which drowsiness and powerlessness come on early, are succeeded by tetanic spasms, the other symptoms also being present, and later, persistent enteritis with loss of the hair on recovery. In 1 case coma was the prominent symptom, with death on the sixth day.

When antimony chlorid has been taken, to the symptoms of antimony-poisoning are added those of the strongly acid liquid, which causes corrosion of the stomach.

Chronic Poisoning.—In most cases of homicidal poisoning from antimony, tartar emetic has been given in divided doses to invalids. The effects of the poison are thus mistaken for symptoms of some low fever or chronic disease, and the crime may go undetected. The patient is seen to suffer from "sickness," loathing for food, which, if taken, is not retained, diarrhea, muscular cramps, physical and nervous prostration, weak pulse, and cold sweats.

Fatal Dose of Tartar Emetic.—The smallest dose that has proved fatal to a child is $\frac{3}{4}$ gr. (48.5 mg.). A healthy woman, aged twenty-five years, took the maximum medicinal dose, $1\frac{1}{2}$ gr. (97.2 mg.), without effect, but a similar dose twenty-four hours later excited violent purging and vomiting, with death in thirty-six hours. Such cases cannot be considered as fixing the danger limit. Ten grains at one time would be a dangerous dose, but the same amount in broken doses would be still more so.

Recovery has followed a dose of 170 gr. As a rule, prompt emesis follows the administration of a large dose, and the effects are mainly local and not serious. If the poison be retained and absorbed, the vomiting center is indirectly involved, and purging, with extreme depression, becomes the prominent symptom. At one time it was considered good practice in acute inflammatory diseases to give doses of 1 gr. at intervals, to establish "tolerance." By the second day some patients would tolerate the drug without vomiting and purging, and "heroic" doses of 5 gr. each could be given without inducing these effects. As much as 60 gr. daily have been given in this way without disturbance of the stomach. The effects in such cases are mainly those of depression of the heart action and of the nervous system.

Fatal Period.—A fatal result has occurred in an adult in seven

hours. In an exceptional case death occurred in a child in three-quarters of an hour. The fatal event may be delayed for several days, the average duration of life being twenty-four hours.

Treatment.—As a rule, the free vomiting induced by the tartar emetic is sufficient to evacuate the stomach. In the rare cases where it does not occur, other emetics should be given, such as sulphate of zinc or mustard and water; or the stomach may be washed out with a mixture of hot water with the antidote, tannic acid; or a decoction of green tea or of some vegetable astringent—all these forming the insoluble tannate of antimony. When the stomach has been emptied morphin should be given hypodermically to relieve pain, and the irritable stomach and bowels treated with suitable remedies. The depression of the heart must be counteracted with stimulants, aided by dry heat or mustard to the epigastrium and the extremities.

If antimony chlorid has been taken, the corrosive action on the stomach would cause a condition which would be aggravated by the mechanical irritation of the stomach-tube.

Postmortem Appearances.—In 1 case of acute tartar-emetic poisoning the autopsy revealed nothing, although the poison was found in the viscera, urine, blood, and intestinal contents. Such a result is quite exceptional, most cases showing redness, swelling, ecchymotic patches, and perhaps ulceration in the gastro-intestinal mucous membrane. Sometimes the changes in the gullet and pharynx are profound, as in a case in which there was destructive ulceration of the membrane of the epiglottis and of the adjacent parts, exposing the muscular fibers of the pharynx. In a case of poisoning from the corrosive antimony chlorid, after vomiting without blood, the patient went into collapse and died in two hours. The gastric membrane was almost black from congestion.

In cases of chronic poisoning it is usual to find inflammation of the kidneys and liver.

When heated in a test-tube tartar emetic chars, and later gives an amorphous sublimate of Sb_2O_3.

Tests.—Hydrogen Sulphid.—A stream of this gas will precipitate orange-red antimony trisulphid, Sb_2S_3, when passed through any antimonial aqueous solution acidified with hydrochloric acid (Plate 2, No. 5). This orange precipitate is insoluble in ammonium hydroxid, but dissolves in the fixed alkalis, in ammonium sulphid, and in strong hydrochloric acid, especially when heated. A very characteristic reaction is obtained when this hydrochloric acid solution (after boiling to expel all trace of hydrogen sulphid) is diluted with excess of water. A white precipitate of antimony oxychlorid falls, which is soluble in tartaric acid.

Fallacies.—While this test is quite certain in simple solution, it may give a doubtful result in the presence of colored organic materials. These should be entirely destroyed to give a satisfactory verdict.

Delicacy.—A definite reaction can be obtained with $\frac{1}{10000}$ of a grain of antimony trioxid in 5 gr. of solution.

Reinsch's Test.—The method of performing this test has been described in another place (p. 277). If any precipitate form, when the suspected solution is acidified with hydrochloric acid, more acid must be added until the oxychlorid is redissolved. On boiling in it a strip of bright, pure copper-foil a film of metallic antimony will appear. If the amount be small, the film is violet. A larger quantity will give a surface like tarnished zinc, and, if abundant, a black amorphous layer.

Fallacies.—Arsenic, mercury, and some other metals make similar deposits. To distinguish the nature of the metallic films the copper strip must be washed in water, alcohol, and ether, dried, coiled, and heated in a glass tube open at both ends. Under this treatment antimony yields a white sublimate of antimony trioxid which is usually amorphous, although sometimes showing crystals; arsenic gives a sublimate of octahedral crystals; mercury a sublimate of shining metallic globules; and other metals, as a rule, produce no sublimate. The antimony trioxid may be dissolved in weak tartaric acid and an orange-red precipitate be obtained by passing hydrogen sulphid after acidification with hydrochloric acid. Again, the film of antimony on copper may be identified by boiling it in a weak solution of potassium hydroxid, removing the strip at intervals to expose it to the air. If the solution of antimony thus made is acidified with hydrochloric acid, it will yield an orange-red precipitate with hydrogen sulphid.

Delicacy.—A distinct violet-colored deposit on the copper can be obtained from 1 gr. of a solution containing $\frac{1}{20000}$ gr. of tartar emetic, or $\frac{1}{50000}$ gr. of antimony trioxid.

Marsh's Test.—In the section on Arsenic (p. 279) details are given for performing this test. If antimony be present the gaseous terhydrid will be formed which has not the onion-like odor of arsenic terhydrid. Its flame produces a black spot on cold porcelain, while a metallic mirror forms in the delivery tube if that be heated by Berzelius' method. These may be mistaken for the similar deposits made by arsenic. When treated with solution of chlorinated lime or chlorinated soda the antimony deposit is insoluble, while arsenic dissolves. Yellow ammonium sulphid dissolves both, but on evaporation the solution of antimony sulphid leaves an orange-red spot soluble in strong hydrochloric acid, but insoluble in ammonia. The corresponding

arsenic sulphid is yellow, insoluble in hydrochloric acid, but soluble in ammonia.

If the gas, instead of being burned or decomposed by heat as above, be passed into solution of silver nitrate, there is a black deposit of silver antimonid, Ag_3Sb. If arsenic be also present, it remains in solution and, by filtration, we can separate the two. The filtrate can be tested for arsenic. The antimony in the precipitate may be separated from the silver by dissolving in boiling, weak hydrochloric acid. When filtered again and treated with hydrogen sulphid the filtrate gives orange-red antimony sulphid.

Delicacy.—With a small apparatus spots on porcelain are obtained from 50 gr. of a fluid containing $\frac{1}{200}$ gr. of antimony trioxid, while a good deposit in the heated tube is yielded by the same amount of fluid containing $\frac{1}{1000}$ gr. of antimony trioxid.

The **silver nitrate test** gives a still more delicate reaction, and can be obtained with only a few drops of the test solution, a satisfactory deposit of silver antimonid forming when there is present only $\frac{1}{8000}$ gr. of tartar emetic, equal to $\frac{1}{20000}$ gr. of antimony trioxid.

Zinc Test.—The suspected liquid is put into a platinum dish and acidified with hydrochloric acid. On immersing a slip of pure zinc the antimony, but not arsenic, is at once deposited on the platinum as a black stain, which can be removed later by nitric acid or by simple heat. The true nature of this stain is revealed by wetting it with nitric acid, drying at a gentle heat, and touching with a drop of dilute ammonium sulphid, when an orange-red color will be produced, due to the formation of antimony trisulphid.

Delicacy.—This test is very delicate. In two minutes a brown stain will appear when the solution holds but $\frac{1}{10000}$ gr. of antimony, a definite reaction showing in a quarter of an hour when the amount is only $\frac{1}{200000}$.

Tin Test.—If an antimony solution be acidulated with $\frac{1}{10}$ part hydrochloric acid and a slip of pure tinfoil is immersed in it, the foil turns black from a deposit of metallic antimony.

Detection.—In Vomited Matters and Urine.—Owing to the prompt action of tartar emetic, the stomach and bowels are usually quickly evacuated of the poison. A large part of that which is absorbed into the general circulation is rapidly eliminated by the kidneys, and hence the proportion stored in the viscera is relatively small. In cases of suspected chronic poisoning the vomited matters, the liquid feces, the urine, or medicinal mixtures should be subjected to analysis. For this purpose the material is acidified with hydrochloric acid, and the zinc test or Reinsch's test applied. These respond even in the presence of organic matter. To another portion of the material, acidified with hydro-

chloric acid, tartaric acid is added; it is heated on a water-bath for half an hour, strained, filtered, and the filtrate treated with a stream of hydrogen sulphid for several hours. The precipitate, which may contain the sulphids of certain other metals and free sulphur, should be treated with strong hydrochloric acid and boiled as long as hydrogen sulphid fumes escape. The filtered solution may be tested with Reinsch's test, the zinc test, or Marsh's test, collecting the antimony in silver nitrate solution. In testing the urine the total quantity for several days should be evaporated to a small bulk before being operated on.

Separation from the Tissues.—From the solid viscera most of the antimony can be extracted by mincing a portion and boiling it for an hour in water, 5 parts, acidified with hydrochloric acid, 1 part. The strained and filtered solution may be tested by Reinsch's or the zinc test.

Quantitative Determination.—If it be desired to calculate the total amount of antimony, it is best to use the process for destruction of organic matter by hydrochloric acid and potassium chlorate given in another place (p. 284). This being done, the mixed precipitate obtained by passing hydrogen sulphid through the acidified fluid is washed, treated with strong nitric acid, and evaporated to dryness. A small quantity of a strong solution of potassium hydroxid is added to the residue, it is filtered, evaporated to dryness, and fused. The potassium antimonate in this fluid is boiled with solution of tartaric acid, acidulated with hydrochloric acid, filtered, and saturated with hydrogen sulphid gas. The orange-red antimonic sulphid, Sb_2S_5, thus obtained is washed on a Gooch filter,[1] dried in a water oven, and the free sulphur and residual moisture which are always present expelled by heating in an atmosphere of dry carbon dioxid. Of this residue, which has been converted to black sulphid, Sb_2S_3, 100 parts represent 71.77 of antimony.

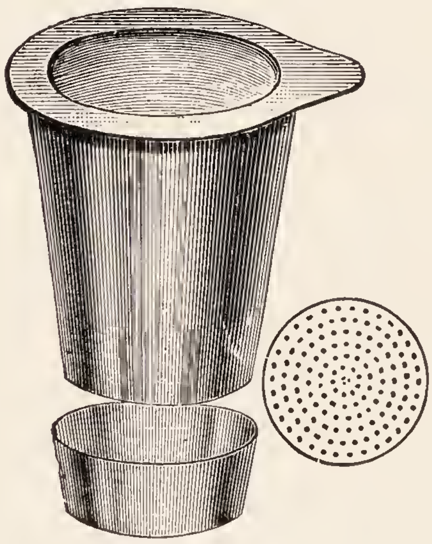


Fig. 68.—Gooch filter or funnel.

When the presence of other poisonous metals is suspected the precipitate made with hydrogen sulphid is treated thoroughly with yellow ammonium sulphid and the solution filtered. The arsenic or antimony is present in this filtrate, while mercury, lead, and copper remain upon the filter to be examined by

[1] A Gooch filter is one in which filtration is effected through an inner lining of asbestos felt, which has been introduced into the perforated bottom of a platinum or porcelain crucible. The precipitate, filtered and washed in the usual way, may be dried and ignited without being removed from the crucible.

appropriate methods. The filtrate is evaporated, and the residue treated with nitric acid and potassium hydroxid to convert the metals into potassium arsenate and antimonate. If the presence of both metals be suspected, this mixture is put into the sulphuric acid and zinc Marsh apparatus, and the gas passed through silver nitrate as long as a black precipitate falls. The arsenic will be in the solution, and is separated by filtration. The black antimonid of silver is collected on a filter, washed, boiled with tartaric acid, acidulated with hydrochloric acid, filtered, and the filtrate precipitated with hydrogen sulphid. Of the dried precipitate of orange sulphid, 100 parts represent 196.47 parts of pure crystallized tartar emetic.

TIN (Stannum)

Symbol, Sn. Atomic weight, 119.

The commercial metal is obtained from *tin stone*, SnO_2, by reduction with coal. It is a silver-white metal, melting at 228° C. (440° F.), and does not tarnish in the air. It is used as pure *block tin;* in *tin-plate*, sheets of iron coated with thin layers of tin; *tinfoil*, thin leaves sometimes containing lead; *tin amalgam*, silver coating for mirrors. It resists the action of air and water so well that vessels coated with it are universally used in the household. It is present in many forms of bronze as alloys with copper, in Britannia metal, alloyed with antimony, and in *soft solder*, alloyed with lead.

Tin forms two series of compounds which are examples of its divalence and tetravalence. The first series are compounds of *distannion*, Sn^{++}, which is colorless and poisonous. They are called *stannous*, as that formed by the action of hydrochloric acid on tin, *stannous chlorid*, $SnCl_2$. This is a strong deoxidizing agent, tending to pass over into the stannic condition, taking two more electric charges, and reducing arsenic, mercury, and gold salts to the metallic state. Dyers use it in calico printing. To check the tendency to become turbid, its solutions are kept stannous by a piece of metallic tin kept in the bottle. It makes a clear solution with one-third volume of water, but turns to white hydroxid, $Sn(OH)_2$, with more water unless HCl is added. On standing it absorbs oxygen and deposits the white oxychlorid. *Stannic chlorid*, $SnCl_4$, contains *tetrastannion*, Sn^{++++}, which is the more stable ion. It is a fuming yellow liquid which tends to gelatinize by forming the hydroxid, $Sn(OH)_4$. It is formed by the action of nitromuriatic acid on tin, or of free chlorin on stannous chlorid. With a molecule of free chlorin the cation takes

up more positive electricity, the atoms of chlorin becoming ionized.

$$Sn^{++}, Cl^-, Cl^- + Cl_2 = Sn^{++++}, Cl^-, Cl^-, Cl,^- Cl^-.$$

Toxicology.—Though poisoning from tin salts is rarely reported, there is sufficient evidence to prove that it does occur.

Putty powder, a higher oxid of tin, was the cause of death in the case of a chemist who, by mistake, used it for months in his pepper-box. The solder used for fruit-cans contains tin with lead. This, as well as the tin surface, may be dissolved by the action of acid juices of fruits or the fatty acids of meat and cause toxic symptoms. In the case of canned meats the danger from this source is slight, as the compound usually formed is insoluble in the digestive juices. The traces found in canned meat and fish exist as oxid, though in rare cases it is a basic stannous chlorid and sometimes a sulphid. The corrosion of the tin may increase slightly after the second year, but the amount is never anything but slight, even after four years.

Symptoms.—Tin salts act as gastro-intestinal irritants, causing sometimes a metallic taste, usually nausea, vomiting, abdominal pain, diarrhea, cyanosis, and collapse. Severe symptoms like these were seen in 4 cases, due to eating tinned cherries, the strongly acid juice in the can showing 3.2 gr. of malate of tin to the fluidounce.

In an investigation upon the lower animals it was shown that even the non-irritating salts given subcutaneously, caused toxic symptoms like those of other metals which undermine the health, sometimes even causing death. Tin was found in the tissues and the urine. Motor and sensory disturbances were noted in the lower extremities of a young woman whose skin was at the same period stained yellow from wearing yellow silk stockings. More marked nervous symptoms, like ataxia, were noted a few weeks later, simultaneously with wearing the stockings. The urine was albuminous, and gave the tin reaction for two months after the stockings had been laid aside. The stockings were heavily impregnated with tin chlorid to give them "body," and the absorbed tin had produced marked anemia. With the exception of hysteric symptoms, the patient recovered in a few months.

Treatment.—Emetics and the stomach-pump should be used first, followed by eggs, bland demulcent drinks, stimulants, and anodynes.

Tests.—**Hydrogen sulphid** yields with stannous solutions brown stannous sulphid, SnS, with stannic solutions, yellow stannic sulphid, SnS_2 (Plate 2, No. 6). Both precipitates are soluble in ammonium sulphid.

Mercuric chlorid is reduced by stannous chlorid to a gray deposit of metallic mercury. The reduction takes place in two stages. At first a white precipitate falls of mercurous chlorid and later this is reduced to the metallic state.

$$HgCl_2 + SnCl_2 = Hg + SnCl_4.$$

Solutions of fixed alkalis give with stannous salts a white precipitate of hydroxid, $Sn(OH)_2$, which is dissolved by excess, and on boiling is reprecipitated as black oxid. With stannic salts the white precipitate is stannic acid, H_2SnO_3, and when dissolved is not reprecipitated by boiling.

Detection.—To extract the metal from the tissues and organic fluids they should be boiled for some time in water acidulated with hydrochloric acid, filtered, and the above tests applied to the filtrate.

V.—THE COPPER GROUP

Copper, mercury, lead, bismuth, silver, and cadmium belong to a group of heavy metals whose sulphids are insoluble in water, dilute acids, or ammonium sulphid.

COPPER (Cuprum)

Symbol, Cu. Atomic weight, 63.57.

Occurrence.—Copper is found in the free condition; as *cuprite* or oxid; *azurite* and *malachite*, the blue and green carbonates; and as *copper pyrites*, $CuFeS_2$. By processes of roasting and reduction the metal is obtained from these ores and finally purified by electrolysis in a bath of its sulphate, using impure copper as an anode.

Wide Distribution in Nature.—Not only is copper to be found in native masses and in its ores, but in minute proportions it is a constituent of many common minerals and soils. Natural water takes up a trace, and vegetation thus derives it from soil and from water. Careful analysis has detected it in edible roots, such as the turnip, in fruits, berries, salads, wheat, barley, and other cereals, coffee, chocolate, and quinin. From plants as food it is found to be derived by animals—domestic and wild. Even oysters sometimes show a trace. Constantly present in our chief foods, it is not surprising that it is found in the body of man. Leaving out of the count foods possibly contaminated artificially, it is estimated that each of us takes daily about 1 mg. (0.015 gr.) of cop-

per. At the same time it is not a physiologic constituent of the body, like iron.

Physical Properties.—Copper is a heavy, bright-red solid which in moist air becomes coated with a green carbonate. It soon loses its red luster, taking a brown coat of oxid or sulphid. When heated it oxidizes in air to form a black oxid. Copper is of value in the arts because it is strong, malleable, ductile, a good conductor of electricity, and a resistant to most reagents, under ordinary conditions.

Brass is an alloy of about 2 parts copper to 1 of zinc.

Bronzes contain copper, tin, and sometimes zinc.

Bell metal is an alloy of copper and tin.

Phosphorus bronze is a copper bronze containing phosphorus.

Aluminium bronze, which is yellow and resembles gold in appearance, is an alloy of copper and 8 per cent. aluminium.

German silver is an alloy of copper, nickel, and zinc.

Coin silver contains 10 per cent. of copper.

Copper dissolves in nitric acid, in hot sulphuric acid, and, when exposed to the air, in hydrochloric acid and in ammonia. Even distilled water will in time take up some. One hundred cubic centimeters may dissolve 0.3 mg. of copper or 0.2 gr. in 1 gal. Water kept a few hours in a brightly polished copper vessel takes up the metal as *colloidal solution* in amounts harmless to man, but distinctly bactericidal. Natural waters containing salts, especially the chlorids, exert still more solvent powers. The syrups and fats dissolve it, and the fatty acids readily combine with it. Vinegar, acid wines, and subacid fruits kept for a few hours in copper vessels are found to contain the metal.

The Ions of Copper.—Two series of copper salts are known, called respectively *cuprous* and *cupric*. In the cuprous salts the ion is univalent, *monocuprion*, Cu^{+}; in the cupric it is bivalent, *dicuprion*, Cu^{++}. The latter condition is the more stable, and is characterized by the blue color of its salts. It is not poisonous, but some of its salts are irritants in large doses.

When a piece of zinc is immersed in a copper sulphate solution the copper ion Cu^{++} yields its two charges to an atom of zinc and is deposited as an atom; the zinc taking the charges passes from the atomic to the ion state as zinc sulphate in solution.

$$Cu^{++}, (SO_4)^{=} \quad + \quad Zn \quad = \quad Zn^{++}, (SO_4)^{=} \quad + \quad Cu.$$

This is the second mode of ion formation, which consists in a simple transference of electricity from metal to metal.

Electrolytic Solution Tension.—A metal immersed in an aqueous solution exerts a pressure which tends to send off ions from the

metal into the solution. This solution tension is high with zinc, which has a great tendency to ionize, but lower with copper, which, therefore, gives place to the zinc. It is a general principle that *metals with great solution-tension precipitate from their salts those that have less* (p. 90).

Oxids.—The two ions are represented in the oxids: cuprous, Cu_2O, and cupric, CuO.

Cuprous oxid is the red powder precipitated in Trommer's test for glucose. A hot alkaline solution of a cupric salt is reduced red by the sugar in simple solutions, but in urine the precipitate is yellow or yellowish red (Plate 8, Fig. 3).

Cupric oxid is the black coating formed on metallic copper when heated to dull redness in oxygen or air. If the oxid be heated to a higher degree in the presence of hydrogen it gives up the oxygen to form water.

Cupric Hydroxid ($Cu(OH)_2$).—When a copper salt is acted upon by an alkaline hydroxid, a light blue precipitate is formed. It remains insoluble in potassium and sodium hydroxids, but in an excess of ammonium hydroxid it passes into solution with a deep sapphire-blue color. A new ion, *cuprammonium*, $Cu(NH_3)_4^{\cdot\cdot}$, has been produced, in which ammonia as a constituent persists even when the salt has been separated as a dark blue solid. In performing Trommer's test without glucose, the addition of potassium hydroxid precipitates the blue hydroxid:

$$CuSO_4 + 2KHO = Cu(HO)_2 + K_2SO_4.$$

When heated, the turbid blue fluid turns black, as the hydroxid changes to cupric oxid:

$$Cu(OH)_2 = H_2O + CuO.$$

But if glucose be present, oxygen is taken out and red cuprous oxid formed (Plate 8, Fig. 3), in accordance with this equation:

$$2Cu(OH)_2 = 2H_2O + O + Cu_2O.$$

Cuprous chlorid, $CuCl$, is formed when hydrochloric acid is treated with excess of copper and the result added to water. It absorbs oxygen, changing to cupric chlorid and also carbon monoxid, forming $Cu_2Cl_2CO \cdot 2H_2O$.

Cupric chlorid, $CuCl_2$, is formed when cupric hydroxid is dissolved in hydrochloric acid: $Cu(HO)_2 + 2HCl = CuCl_2 + 2H_2O$.

In concentrated solutions it is only slightly dissociated and, therefore, has the greenish-yellow color of the $CuCl_2$ molecule;

but when the solution is diluted, and thereby the dissociation increased, the blue color of the Cu^{++} ions appears. By heating this blue solution or by adding excess of chlorin the dissociation is driven back and the blue turns green and finally yellow.

Copper sulphate, $CuSO_45H_2O$, commonly known under the trivial name of *bluestone*, occurs in large, blue, slightly efflorescent crystals, freely soluble in water, and having a strong metallic taste. The blue color is explained by the dissociation of the blue cupric ion in the water of crystallization. When heated the water is driven off and the anhydrous salt is white. It is used in medicine as an external application for its astringent or mild stimulating qualities. Internally, in doses of ¼ to 2 gr., it is given as a tonic and astringent; in doses of 5 to 10 gr. it acts as a prompt emetic. It is employed in phosphorus-poisoning as an antidote and also as an emetic. In very large doses it is poisonous, and has been used both for suicidal and for homicidal purposes.

Copper subacetate, $Cu2C_2H_3O_2$, CuO, is prepared by treating metallic copper with acetic acid in the air. It crystallizes in blue-green prisms. In an impure form it is known as *verdigris*. The same name is popularly given to other green salts of copper, as the oleate and carbonate. Verdigris in medicine is used only externally. In the arts it is frequently employed.

Toxicology.—The **irritant salts** are copper sulphate (*blue vitriol*), copper subacetate (*verdigris*), and copper aceto-arsenite (*Paris green*). As the poisonous properties of the last named are dependent chiefly upon the arsenic, it has been considered among the compounds of that metal (p. 291).

Metallic copper is not poisonous, as is demonstrated by the use of copper wire for surgical sutures and the absence of injurious consequences when a copper coin is swallowed. When used for sutures copper wire is found to exert a powerful inhibitory action on bacteria; in fact, much greater than that of any other metal.

Symptoms of Acute Poisoning.—Out of 8 cases registered in England in ten years, 3 were suicidal, 5 were accidental, and none was homicidal. The very disagreeable taste of copper salts prevents the criminal use. The onset of the symptoms may be said to begin with this coppery astringent taste and the feeling of tightness in the throat. In a few minutes nausea and violent vomiting of greenish matters begin. Soon appear thirst, pain in the stomach, and colic, with violent purging of stools having the same green hue of the vomit. Ammonia-water added to the green excreta will turn them blue, and thus distinguish this copper-green from bile. The urine is scanty and may become albuminous, inky from changed hemoglobin, and loaded with tube-casts. The later stages are characterized by nervous phenomena, such as pains,

spasms which may be tetanic, paralysis, delirium, and collapse. In the course of a few days jaundice appears as a result of involvement of the liver.

Fatal Dose.—Owing to the energetic emetic properties of large doses of copper sulphate, evacuation of the stomach is so prompt that we have no means of determining how much would prove fatal. On the one hand, a child four and a half years old has recovered after a dose of over ½ oz. of copper sulphate; on the other hand, an adult has succumbed to a dose of ½ oz. of verdigris.

Fatal Period.—As a rule, life is prolonged for several days, the patient sometimes almost recovering from the symptoms of gastro-enteric irritation and finally dying from the effects of the absorbed poison. Copper sulphate has caused death in four hours.

Treatment.—Evacuation of the stomach must first be obtained by stimulating the natural effort at vomiting. The antidote is the albumin of egg or the casein of milk. Eggs beaten in warm water should be given freely. If vomiting does not occur or is not active, the stomach-pump should be resorted to and the stomach washed out with milk or eggs and water. A milk diet with castor oil will favor removal from the intestine.

Postmortem Appearances.—Congestion, swelling, softening, and excoriations of the mucous membrane of the stomach and bowels are usually found. The colon sometimes shows large ulcerations. A bluish discoloration of the lining membrane indicates that all the copper has not been evacuated. The liver may be soft and fatty, the kidneys swollen, and the tubules closed with bloody casts.

Chronic Poisoning.—Until comparatively recent times it was thought that the slow introduction of minute doses of copper was injurious to the tissues by causing such pathologic changes as are known to be due to certain other poisons, such as phosphorus, arsenic, antimony, lead, and mercury. It has been proved that as a slow poison copper belongs to a different category—that of silver and zinc. To produce toxic phenomena it must be given freely and intentionally. After a long course there are functional disturbances of the muscular and nervous systems, anemia, and cachexia. As soon as the administration ceases the functions are restored and the subject spontaneously recovers from the cachexia. It has not been demonstrated that any doses, however large, which have been taken with food have ever caused death, while medium doses in the beginning act as simple emetics, tolerance is rapidly established, and administration can be continued for six months with little impairment of health.

Copper salts are extensively used to impart a lively green color to pickled cucumbers and canned peas and beans. An

insoluble green compound is formed between copper and acid phyllocyanic from the chlorophyl in the vegetable. Elaborate researches have been carried out in various countries under the highest sanitary authorities to settle the limit of copper admissible as not injurious to health. The U. S. Dept. of Agriculture, Board of Food Inspection maintains (1913) that copper sulphate used for the greening of vegetables is injurious, regards as adulterated all foods so treated, and forbids their importation or shipment by interstate commerce. (See Food Inspection Decision 149, Washington, D. C., Dec. 26, 1912.)

At one time it was generally believed that workers in copper or its compounds, such as malachite, were liable to a disease called "copper colic," which differed from lead colic in that diarrhea was present instead of constipation; there was greater prostration, its duration was shorter, and the prognosis was good. It is now maintained by able investigators that such symptoms are not due to copper, but to the lead and arsenic which are impurities in most ores and in the commercial metal, or to the lead in the solder used by the operator. This is borne out by the fact that after more than one attack "wrist-drop" or lead-palsy is apt to supervene. No symptoms of poisoning are found in certain copper workers who show copper as a purplish or bluish line on the gums, whose hair turns green, and whose urine stains the ground green. "The contention that there is no chronic copper poisoning in men or animals (comparable to lead or mercury) is at present uncontradicted."

Tests.—Hydrogen Sulphid Test.—A stream of hydrogen sulphid passed through an acid solution of a copper salt yields a brownish precipitate of copper sulphid, freely soluble in warm nitric acid, slightly so in excess of ammonium sulphid, but insoluble in the caustic alkalis.

Ammonia Test.—A solution of a copper salt is either green or blue. By adding ammonium hydroxid in excess to a slightly colored solution, cupric hydroxid is formed and dissolved to make a much deeper sapphire-blue solution.

Fallacies.—The salts of nickel give the same deep blue solution.

Delicacy.—The change in color is recognizable in 1 gr. of a solution containing $\frac{1}{5000}$ gr. of copper oxid.

Potassium Ferrocyanid Test.—This reagent precipitates from a strong copper solution the reddish-brown copper ferrocyanid. When the solution is very dilute no precipitate falls, but the solution turns reddish brown. The brown precipitate is insoluble in acetic and hydrochloric acids, but with ammonium hydroxid forms a greenish-blue liquid.

Fallacies.—Solutions of uranium salts yield a similar brown precipitate, but when this is treated with excess of ammonium hydroxid the liquid is yellow, not blue.

Interferences.—A trace of iron will give a blue color with this reagent and thus mask the result.

Delicacy.—A distinct red reaction can be obtained from $\frac{1}{25999}$ gr. of copper oxid.

Iron Test.—This test separates copper in the metallic state. It is performed by immersing a steel needle or other piece of bright steel or iron in the suspected liquid slightly acidulated. If copper be in solution, it will be deposited as a reddish layer on the iron. The *solution tension* of iron is much higher than that of copper; hence, the ions of copper give place to the iron and are precipitated as metallic molecules. To prove that this film is copper it is dipped in ammonium hydroxid and exposed to the air, when the film of copper turns blue.

Galvanic Zinc Test.—Very delicate results can be obtained by immersing in a copper solution a galvanic couple made by wrapping platinum wire around a piece of zinc-foil. The platinum is soon discolored by a deposit, the nature of which can be established by exposing it to the vapors arising from potassium bromid when treated with sulphuric acid. The deposit changes in color, and if rubbed on white porcelain leaves a violet mark.

Electrolytic Test.—Having obtained the copper in solution and concentrated it, make it acid with hydrochloric acid and put it in a weighed dish of platinum which is connected with the zinc pole or cathode of a battery. A strip of platinum-foil as anode is immersed in the tested solution for twenty-four hours. In that time all the copper will be deposited on the platinum dish. To make a quantitative estimate the dish must be washed, dried, and weighed again. The gain represents the total amount of copper in the volume of tested solution.

Separation of Copper from Animal Matters.—The organic matter in the contents of the stomach, or in the liver, brain, or other tissues, must be destroyed by burning to an ash and extracting with nitric acid, or boiling with hydrochloric acid and potassium chlorate, according to the systematic procedure given on p. 283. By evaporation the excess of acid can be removed, and the residue, dissolved in acidulated water, may be tested by the methods given above.

MERCURY (Hydrargyrum)

Symbol, Hg. Atomic weight, 200.

Occurrence.—Quicksilver is found native, but the chief source is the sulphid ore, *cinnabar*, HgS. By simple heat the sulphur

oxidizes to SO_2 and the volatile metal vaporizes, to be collected as a distillate.

Amalgams.—Mercury is a solvent for gold, silver, zinc, metals of the alkalis, and the alkaline earths and many other metals. This mercurial solution is called an *amalgam* of the metal dissolved.

Physical Properties.—Mercury is the only metal that is in the liquid state at ordinary temperatures. It freezes at $-39.4°$ C. ($-40°$ F.), and boils at 357° C. (675° F.), but at all ordinary temperatures it vaporizes spontaneously. Having this great range of fluidity joined to the high density of 13.595, and not wetting glass, it is invaluable in the construction of barometers, thermometers, manometers, and other scientific instruments.

Chemical Properties.—Mercury retains its silver-white, metallic luster in the air, because it combines with oxygen only at high temperatures. It unites directly with chlorin and the other halogens at ordinary temperatures.

The Ions of Mercury.—Mercury forms two series of salts, *mercurous* and *mercuric*, in which the anions of acids are combined with two different elementary ions of mercury. In one series the mercurous ion (*monomercurion*), Hg^+, is univalent; in the other the mercuric ion (*dimercurion*), Hg^{++}, is bivalent. With an excess of metallic mercury the product of the action of an acid such as nitric is mercurous. Without that excess the mercurous nitrate passes to the condition of mercuric. Both ions are poisonous to bacteria and animal life. In the body the mercurous ion forms with chloridion a mercurous salt of low solubility and, therefore, of feeble powers, but the mercuric ion forms salts of higher solubility and of greater toxic activity.

The metal is cleansed from impurities that impair its luster and make it "drag a tail" by shaking with dilute sulphuric acid to which a few drops of solution of potassium bichromate are added from time to time. The contaminating metals are oxidized and dissolved and can be washed away.

When metallic mercury is finely triturated the globules remain separate if the trituration has been done in the presence of some substance which gives a coating, such as fatty matter or a confection.

The metal has been given in the pure state to remove obstruction from the bowels mechanically, with no injurious consequences unless retained for a number of days. The metal is present, finely divided, and possibly oxidized in "gray powder" (*hydrargyrum cum creta*), "blue mass" (*massa hydrargyri*), "blue ointment" (*unguentum hydrargyri*). In this condition, and also if inhaled in the state of vapor, the metal is converted by the fluids of the body into active compounds which exhibit all its poisonous

effects. Among its poisonous salts are its oxids, iodids, mercurammonium chlorid, mercuric nitrate, and mercuric chlorid (corrosive sublimate).

Mercurous Oxid (Hg_2O) (*Black Oxid*).—This black insoluble powder is precipitated from solutions of mercurous salts by bases:

$$2HgCl + 2NaOH = 2NaCl + Hg_2O + H_2O.$$

It is unstable, changing in time to mercuric oxid and metallic mercury. Sunlight hastens this conversion:

$$Hg_2O = HgO + Hg.$$

Lotio hydrargyri nigra, or "black wash," is a mixture in which calomel is converted to mercurous oxid by lime-water, leaving calcium chlorid in solution:

$$2HgCl + Ca(OH)_2 = CaCl_2 + Hg_2O + H_2O.$$

Mercuric oxid, HgO, is obtained as a yellow powder by precipitation from mercuric salts with soluble bases.

Hydrargyri oxidum flavum (yellow precipitate) is formed when a solution of mercuric chlorid is poured into a solution of sodium hydroxid:

$$HgCl_2 + 2NaOH = 2NaCl + HgO + H_2O.$$

It is slightly soluble in water, imparting an alkaline reaction and metallic taste.

The color of mercuric oxid depends upon the fineness of division. When precipitated from cold solutions it is yellow; from hot solutions it is orange. In both cases it is finely divided and in consequence energetic.

As the "red precipitate" it is more compact, coarser, and crystalline; its official name then being *hydrargyri oxidum rubrum*. It is obtained by heating either mercurous or mercuric nitrate moderately, oxygen and nitrogen peroxid being driven off and the red oxid left behind:

$$Hg(NO_3)_2 = HgO + 2NO_2 + O.$$

Mercuric oxid is partly dissolved and partly suspended in "yellow wash," *lotio hydrargyri flava*, which is obtained when a solution of corrosive sublimate is poured into lime-water:

$$HgCl_2 + Ca(OH)_2 = CaCl_2 + HgO + H_2O.$$

Oleatum hydrargyri contains 25 per cent. by weight of the yellow oxid.

There is a 10-per cent. ointment of "yellow precipitate," *unguentum hydrargyri oxidi flavi*, and one of "red precipitate" of the same strength, *unguentum hydrargyri oxidi rubri.*

Mercurous chlorid, HgCl (*hydrargyrum chloridum mite, mild chlorid, calomel*), can be made by subliming a mixture of mercuric chlorid and metallic mercury:

$$HgCl_2 \quad + \quad Hg \quad = \quad 2HgCl.$$

Precipitated calomel is a more active form, owing to the fineness of its division. A solution of mercurous nitrate yields mercurous chlorid when acted upon by sodium chlorid:

$$HgNO_3 \quad + \quad NaCl \quad = \quad HgCl \quad + \quad NaNO_3.$$

Calomel is a heavy, white, insoluble, tasteless powder that is not considered poisonous. If retained too long it changes to some more active compound, such as the poisonous mercuric chlorid, and then produces systemic symptoms. It is so extensively used that milder toxic effects are not infrequent, owing to these changes in the stomach or in the prescription, due to incompatible association. It is probable that most of the few fatal cases reported were brought about by the conversion of the calomel by the fluids of the body into some poisonous salt. It is readily oxidized to the mercuric chlorid. It is converted into mercuric chlorid by nitrohydrochloric acid and chlorin-water, and probably to a slight extent also by hydrochloric acid and alkaline chlorids. It is changed to oxid or reduced by the alkaline bases and carbonates. Prolonged exposure to sunlight changes it to metallic mercury and mercuric chlorid, as is shown by this equation:

$$2HgCl \quad = \quad Hg \quad + \quad HgCl_2.$$

The HgCl is of such difficult solubility that few Hg ions are dissociated from it in a brief sojourn in the body, but the $HgCl_2$ is freely soluble, dissociates Hg ions promptly, and, therefore, is more active in every way. Calomel should be kept in opaque containers in order to prevent this change.

It is *incompatible* with halogens, chlorids, bromids, iodids, sulphates, carbonates, hydrates, acids, alkalis, soap, cocain, hydrocyanic acid and cyanids, sulphurous acid, hydrogen peroxid, iodoform, salts of lead, copper, or silver; sugar, tragacanth, acacia, pilocarpin, antipyrin, acetanilid, and sweet spirits of niter.

Dose as cathartic: 5 to 15 gr. (0.33–1.0 gm.); as internal antiseptic, $\frac{1}{8}$ to $\frac{1}{4}$ gr. every hour.

Mercuric Chlorid ($HgCl_2$) (*Hydrargyri Chloridum Corrosivum, Corrosive Chlorid, Bichlorid of Mercury*).—This salt is commonly called *corrosive sublimate*, because it is a local corrosive and is prepared by subliming a mixture of mercuric sulphate and sodium chlorid:

$$HgSO_4 + 2NaCl = Na_2SO_4 + HgCl_2.$$

Corrosive sublimate is usually seen in crystalline masses; it sublimes at 82.2° C. (180° F.), and is deposited in needles, in octahedra, or in stellate aggregations of crystalline plates (Fig. 69).

Fig. 69.—Sublimate of mercuric chlorid, magnified. Stellate crystals.

It has no odor, but an acrid, metallic taste. It is soluble in 16 parts of cold water and 3 parts of boiling water, but is far more soluble in solutions of common salt or other alkaline chlorids, forming salts of the anions $(HgCl_3)^-$ and $(HgCl_4)^=$, such as $Na(HgCl_3)$ and $Na_2(HgCl_4)$, which have less bactericidal power than the simple mercuric chlorid in a concentration containing the same amount of mercury. Mercuric chlorid alone is dissociated very little, as compared with sodium chlorid alone. The double chlorid is dissociated even less. The germicidal power of mercury salts is proportionate to the simple mercuric ion and not to the other

component. Hence, the addition of NaCl to a concentrated solution of $HgCl_2$ locking up some of the Hg in the complex $(HgCl_3)^-$ lessens the number of active Hg^{++} ions and lowers the germicidal power. To make antiseptic solution it is best to use pastilles containing not more than 4 parts of NaCl to 1 of $HgCl_2$ and dissolving only 1 gram per liter. At this dilution the NaCl favors the solution of the $HgCl_2$ without material reduction of germicidal action. In the presence of the organic exudations of a wound, changes occur which cause the dissociation of more mercuric ions to take the place of those taken up by the protein. Mercuric chlorid makes a definite insoluble compound with proteid matter, and is, therefore, fatal to low forms of animal and vegetable life. In the dry powder it is inactive chemically and also as a bactericide. Dissolved in alcohol or ether it has little antiseptic power because in these solvents it dissociates very few Hg^{++} ions. In water it supplies the poisonous mercuric ion and exhibits its reactions very well. A solution of it is used in the household to destroy bedbugs, and by taxidermists to preserve skins and mounted preparations. In antiseptic surgery it is extensively employed in irrigating solutions of 1 : 4000 or even 1 : 1000 of water. As it attacks metals it is not suited for disinfecting metallic vessels or instruments.

It is *incompatible* with sulphurous acid and other reducing agents (which reduce it to calomel), ferrum reductum, arsenous, antimonious, and ferrous salts; formic acid; albumin, gelatin, alkalis; alkaloids; soap; lime-water; bromids; iodids; borax; carbonates, phosphates, hypophosphites, salts of copper, zinc, lead, and silver; syr. sarsaparilla comp.; tannic acid and vegetable astringents. Dose: $\frac{1}{80}$ to $\frac{1}{10}$ gr. (0.00075–0.006 gm.).

Mercurous Iodid (HgI) (*Hydrargyri Iodidum Flavum, Green Iodid, Yellow Iodid, Protiodid*).—An acid solution of mercurous nitrate treated with potassium iodid gives a yellow precipitate of mercurous iodid:

$$HgNO_3 \quad + \quad KI \quad = \quad KNO_3 \quad + \quad HgI.$$

It is a tasteless, almost insoluble, powder which decomposes by sunlight into mercuric iodid and mercury, becoming greenish from the presence of the blue particles of metallic mercury. Thus: $2HgI = Hg + HgI_2$. Mercurous iodid should not be prescribed with soluble iodids or the more energetic mercuric iodid will be formed. Dose: $\frac{1}{6}$ to 1 gr. (0.011–0.066 gm.).

Mercuric Iodid (HgI_2) (*Hydrargyri Iodidum Rubrum, Red Iodid, Biniodid*).—When a solution of potassium iodid is added to one of mercuric chlorid a yellow precipitate falls, which at once

turns red on the side to the light and eventually gets red throughout. This red iodid dissolves on the addition of an excess of potassium iodid:

$$HgCl_2 + 2KI = 2KCl + HgI_2.$$

A brilliant-red, tasteless powder, it is very sparingly soluble in water. When it dissolves in the iodid of potassium, a salt is formed, called *potassium mercuric iodid*, by this reaction:

$$2KI + HgI_2 = K_2HgI_4.$$

This salt does not show the usual chemical reactions of mercury, and is less apt to salivate than simple $HgCl_2$ in doses containing the same amount of Hg. Obviously it dissociates very few simple mercuric ions and is properly regarded as a salt, the anion of which is $(HgI_4)^{=}$. *Nessler's reagent* is prepared by adding potassium hydroxid to this potassium mercuric iodid. It is a sensitive test for ammonia. Dose of mercuric iodid: $\frac{1}{50}$ to $\frac{1}{10}$ gr. (0.0013–0.006 gm.).

Its *incompatibles* are the same as those of mercuric chlorid given above.

Mercuric Sulphid (HgS) (*Vermillion*).—There is no mercurous sulphid, but the mercuric compound is very stable. It is found in the ore *cinnabar*, and can be formed by direct union of the elements. The black precipitate formed on passing hydrogen sulphid through a mercurous solution is not mercurous sulphid, unless as a transient phase. Its final composition is a mixture of mercuric sulphid and mercury:

$$2HgCl + H_2S = HgS + Hg + 2HCl.$$

If the hydrogen sulphid be passed through a mercuric solution, whether acid or neutral, the precipitate is at first white, then yellow, red, and black. These are more or less complex and variable compounds of mercuric sulphid with other mercury salts present. Eventually the mass of sulphid overcomes the other salts and a pure black precipitate of mercuric sulphid remains. This black amorphous sulphid is a less stable modification, which can be made to change by sublimation to the permanent red crystalline form known as *vermillion*.

Mercurous sulphate, Hg_2SO_4, is prepared by warming mercury with strong sulphuric acid. There is evolution of sulphur dioxid, and the sulphate is deposited as a white powder of difficult solubility. This powder is the starting-point in the manufacture

of other mercury salts. It is also used in making standard electric cells.

Mercuric sulphate, $HgSO_4$, is formed when the mercurous salt is heated with excess of sulphuric acid. There is evolution of sulphur dioxid, and the heavy, white, crystalline mercuric sulphate is precipitated. On treating this normal salt with boiling water the yellow *basic salt* is formed, and an acid salt remains in solution. The basic salt has been used in medicine under the name of *Hydrargyri subsulphas flavus* or (*oxysulphate* or *turpeth mineral*). Its formula is $Hg_3SO_4(OH)_4$, and it is sometimes regarded as a compound of the sulphate and oxid. It is a yellow, tasteless, insoluble powder. Dose as an emetic: 3 to 5 gr. (0.2–0.33 gm.).

Mercurous Nitrate, $HgNO_3$, and **Mercuric Nitrate,** $Hg(NO_3)_2$.—When mercury is dissolved in cold nitric acid with excess of the metal, the mercurous salt is formed; if the acid be in excess and be heated, then the mercuric nitrate is the product. The white salts thus obtained dissolve in water containing free acid; but, without the acid, water changes them to an insoluble basic nitrate, with the composition $Hg_3(NO_3)_2(OH)_4$, analogous to the basic sulphate. To prove that the mercuric salt is the product, dilute and add hydrochloric acid. If any mercurous nitrate be present, the white mercurous chlorid will be precipitated and more hot nitric acid is needed.

Liquor hydrargyri nitratis is a liquid containing mercuric nitrate 60 per cent. and free nitric acid 11 per cent. It is a colorless, heavy liquid with a strongly acid reaction, used as an escharotic. *Unguentum hydrargyri nitratis* is its ointment, having a bright citrine color.

Ammoniated Mercury (NH_2HgCl) (*Hydrargyrum Ammoniatum, White Precipitate*).—If mercuric chlorid be added to cold ammonium hydroxid in excess, a white precipitate of mercuric ammonium chlorid forms.

$$HgCl_2 + 2NH_4OH = NH_2HgCl + NH_4Cl + 2H_2O.$$

This tasteless and insoluble powder is dissipated by heat without melting. It is ammonium chlorid, NH_4Cl, in which two hydrogen atoms have been replaced by mercury. A 10-per cent. ointment is official under the name of *unguentum hydrargyri ammoniati*.

When a *mercurous* salt is added to ammonium hydroxid a black precipitate falls which may contain metallic mercury with the salt described above. It is probably a complex mixture in which there exists some *mercurous chloramid*, NH_2Hg_2Cl. By

the same reaction paper wet with mercurous nitrate is blackened by the vapor of ammonia.

Toxicology of Salts of Mercury.—Symptoms.—Corrosive sublimate is the salt to which mercury poisoning can be most frequently attributed. However administered, it is a very active gastro-intestinal irritant. When taken by the mouth, the symptoms usually begin within a few minutes. The onset is never delayed half an hour. There are an acrid, metallic taste, constriction of the throat, retching, and a burning sensation in the gullet and stomach. A white coating forms at once on the shriveled lining of the mouth, the inflammation of the throat may involve the larynx, and acute swelling of the glottis may cause asphyxia. The pain in the stomach is so severe as to cause fainting. It comes on promptly, attended by nausea and vomiting of material streaked with blood, and later on purging and straining with bloody stools. Free hemorrhages occur from the stomach, bowels, or other outlet. The urine is scanty or suppressed, the temperature may be febrile or subnormal, the respiration difficult, the pulse thready and irregular. Death is preceded by collapse, unconsciousness, or convulsions.

Fatal results have followed the application of an alcoholic solution of corrosive sublimate (80 gr. to 1 oz.) to the scalp for ringworm. Two cases resulted fatally, from poisoning, by the external application of an ointment of corrosive sublimate to cure the itch. In these cases, besides the painful local inflammation, in a few days gastro-intestinal symptoms appeared, such as vomiting and purging with tenesmus. In addition, there were stomatitis, fetid breath, fever, scanty urine, and collapse. When the poison is absorbed as a result of irrigation of wounds of the vagina, uterus, or abscess cavities, the digestive organs also are profoundly affected. An early effect is serous diarrhea, which afterward becomes bloody, attended by colic and tenesmus, nausea, and vomiting. The urine is usually albuminous, containing epithelial cells and granular casts. While there may be severe headache, insomnia, dimness of vision, and transient disturbance of the intellect, the mind is usually clear to the end. The pulse grows weaker, the pupils contract, the temperature falls, and sometimes an intense erythema appears. The great frequency of deaths from antiseptic irrigations with corrosive sublimate pleads for its disuse in obstetric practice. Numerous fatalities are due to taking it in the dark by mistake for headache tablets. The New York City Board of Health forbids its sale in the solid state except in the form of colored tablets, each one wrapped in a paper marked "poison," the sealed glass container to be conspicuously marked "poison" in red letters.

Fatal Dose.—It is probable that fatal consequences would follow

doses of 3 to 5 gr. of corrosive sublimate. Recovery has resulted after the administration of 100 gr. under prompt treatment by milk, eggs, and emetics. *White precipitate* or mercurammonium chlorid was at one time regarded as non-poisonous. Several deaths from it have been reported—one from 35 gr. *Red precipitate* has caused acute gastro-intestinal irritation when given in doses of 2 dr. or more. *Acid mercuric nitrate*, intended to be used externally only as an escharotic, has been followed by death after such use, and also when administered internally. The *yellow subsulphate*, or turpeth mineral, used in the treatment of croup, has often caused alarming symptoms. Two doses of 3 gr. each have been sufficient to cause death.

Fatal Period.—Death may occur in half an hour, but commonly life is prolonged for from two to four days, and it may last into the second week.

Treatment.—Vomiting should be encouraged by large drafts of milk containing emetics. The casein, like all albuminous compounds, acts as an antidote. The most convenient *protein* should be given freely. This may be raw eggs, flour paste for its gluten, or blood from a freshly killed fowl, given in milk or water. Magnesia would prove beneficial by conversion of the corrosive sublimate to a less injurious compound. It should not be forgotten that the albuminate of mercury may dissolve in excess of albumin; hence emetics are called for after the antidote has been given. The pain, purging, and tenesmus will require such treatment as is usually given for gastro-enteritis.

Postmortem Appearances.—Some parts of the alimentary canal are sure to show inflammatory change. In the mouth, throat, and stomach there will be patches of congestion and erosion, or the intestines, especially the colon, may be the seat of inflammation. Eventually the kidneys swell and take on acute inflammation.

Even when death has occurred from absorption of the poison as a result of application to the skin or irrigation of abscesses or of wounds, or of the uterus and vagina, the most important lesions are in the digestive tract, especially the colon. There is hyperemia of the mucous membrane, of the colon, with easy detachment of the epithelium, patches of superficial necrosis in some parts, and in others a diphtheritic coating infiltrating the deeper layers. The kidneys show a characteristic acute parenchymatous nephritis. In some cases the peritoneum is slightly injected. The liver shows no marked lesion, but is generally pale and anemic. The other organs may be unaffected.

Chronic Poisoning or Mercurialism.—The operatives in quicksilver mines, mirror-makers, fire gilders, thermometer- and barometer-makers, furriers, and hatters are liable to a chronic disease ending in paralysis, brought about by the daily introduction and accumulation in the system of minute doses of mer-

cury. Some of the milder symptoms have been induced by the incautious use of mercurials in the treatment of secondary syphilis, and by repeated applications to the skin of a weak lotion of corrosive sublimate for cosmetic purposes.

The symptoms shown in chronic mercurial poisoning are often quite complex. Ptyalism, or salivation, is usually present; the secretion of saliva is profuse, and is attended with swelling and tenderness in the salivary glands; the gums become red, spongy, and tender, with occasionally a blue line near the teeth; the tongue is swollen and painful; ulcers form in the mouth, and the breath is very fetid. The teeth are loosened, and the alveolar processes sometimes become the seat of acute periostitis. There is usually loss of appetite, with attacks of nausea and vomiting. In some cases colic and diarrhea are present. Soon supervene depressed energies, loss of weight, anemia, and a peculiar cachexia with eruptions of erythema or eczema. The nervous system is eventually involved, showing attacks of cerebral excitability and insomnia, or perhaps hebetude of mind. In the end a peculiar fine tremor spreads from the tongue and face to the upper and lower extremities. The tendency of these tremblings is to progress from the jerky and intermittent form, brought on by excitement or exertion, to the continuous, which lessens only during sleep. The muscles grow weaker, without loss of electrocontractility.

Disturbances of sensation are common; sometimes neuralgia is a symptom, at times appearing as numbness and tingling in anesthetic patches. Affections of sight and hearing are not infrequent.

The *postmortem appearances* indicate that mercury, like arsenic and lead, has the power to excite a progressive peripheral neuritis. The localized mercurial palsies differ from the lead palsies in that the electrocontractility is unimpaired, there is no atrophy, and the tendon reflexes persist. The characteristic nerve lesion is a destruction of the myelin, with preservation of the axis cylinder. The trophic changes are pigmentary and peri-axile.

Treatment of Chronic Mercurialism.—Improvement usually follows removal of the patient from the surroundings where he was exposed to the poison. Although elimination of a single dose is usually complete in a few days by means of the salivary glands, the kidneys, the intestines, and in less degree by the sweat and milk, still if the period of absorption has been prolonged, as it is in chronic mercurialism, some portion of the poison may be retained, combined with albuminous bodies in an inactive state for many months. To stimulate the process of elimination and to secure the oxidation of the albuminous compound so as to set free the mercury, the bowels should be kept opened, the action of the skin promoted by warm baths, and the best hygienic and

tonic regimen instituted. It is customary to administer potassium iodid in small doses in the belief that it changes the deposited poison into mercuric iodid, which is soluble in excess of the potassium salt, and is by this means conveyed into the excretory fluids. For the paralysis, massage and electricity are indicated; for the salivation, mild mouth-washes of potassium chlorate or borax are called for.

Tests.—Sublimation Test for Compounds in the Solid State.—The suspected solid is first thoroughly dried, mixed with dry sodium carbonate, and heated gently in a reduction tube. A shining ring forms on the inside of the tube in the cooler part. A lens resolves this sublimate into minute shining spheres of metallic mercury. The corresponding sublimate of arsenic and

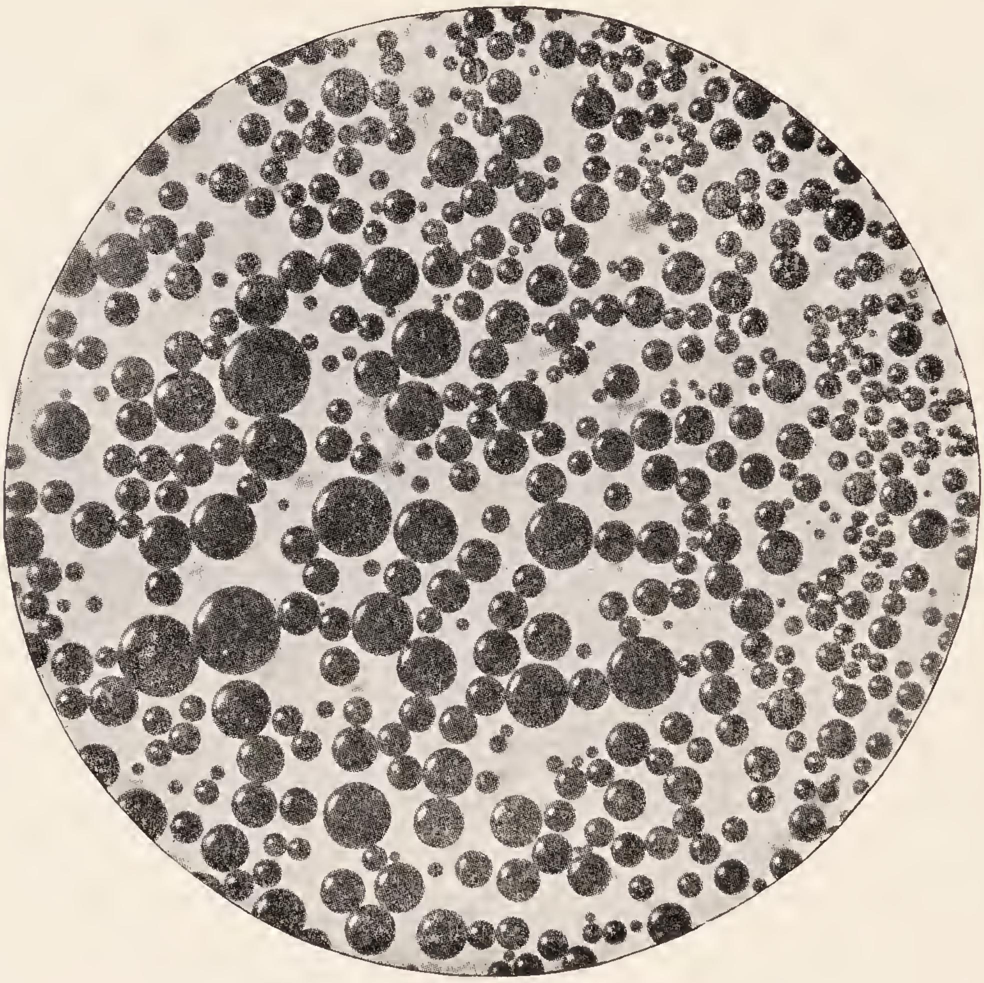


Fig. 70.—Sublimate of metallic mercury, magnified.

antimony are not of this shape. Rubbed with a glass rod, these globules run together into larger rounded masses. A few scales of iodin left in the closed tube for a few hours will vaporize and convert the mercury into a film of yellow, and later of red, mercuric iodid. If this test be done in a small subliming cell, such as is described under Arsenic (p. 277), and collected on a slide for microscopic examination, it is of very great delicacy (Fig. 70).

Hydrogen Sulphid Test.—A solution of a mercurial salt acidulated with hydrochloric acid yields a black precipitate when treated with a stream of hydrogen sulphid. The formation of the mercuric sulphid through intermediate stages is shown if the

tested solution is strong; the precipitate becomes successively yellowish white, dark yellow, orange, brown, and black. The precipitate is insoluble in caustic alkalis, alkaline sulphids, and nitric or hydrochloric acids. It can be identified by yielding the globular sublimate when dried and heated with sodium carbonate, as directed above. By drying the sulphid in an air oven and weighing, the quantity of mercury can be calculated.

Reinsch's Test.—The procedure is the same as that given under Arsenic (p. 277). A strip of bright, pure copper-foil will receive a gray or silvery deposit in a few minutes from a boiling mercurial solution acidified with hydrochloric acid. Having carefully washed the coated copper in water and dried it, the slip should be heated in a small dry reduction tube, and the resulting sublimate examined for globules, as stated above, and tested with free iodin.

Fallacies.—This test yields a metallic deposit on copper from arsenic, antimony, bismuth, silver, and some rarer metals. Coatings of arsenic, antimony, and mercury are the only ones that give a sublimate when heated in a reduction tube.

Mercury is peculiar in its opaque globular form and the bright high lights under reflected light (Fig. 70).

Delicacy.—Using capillary reduction tubes of peculiar construction, characteristic globules have been obtained from $\frac{1}{500000}$ gr. of corrosive sublimate; under ordinary manipulation $\frac{1}{100000}$ gr. is nearer to the limit of delicacy.

Galvanic Gold Test.—A band of goldfoil is wrapped about a strip of thin zinc, leaving some zinc exposed, thus making a galvanic couple. Having acidulated the suspected liquid with hydrochloric acid and warmed it, the two metals are hung in it for several hours. A silvery deposit on the gold indicates mercury. After washing the gold successively in water, alcohol, and ether, it may be heated in a reduction tube and the sublimate of mercurial globules produced may be identified, as stated under sublimation test.

Potassium Iodid Test.—On adding potassium iodid to a solution of corrosive sublimate or other mercuric salt a precipitate falls, at first yellow, but rapidly changing to red mercuric iodid. This will dissolve in excess of the potassium iodid.

Distribution in the Tissues.—Riederen gave to a dog in thirty-one days 2.789 gm. of calomel (2.368 gm. Hg.). By analysis he recovered 2.2 gm. of mercuric sulphid (1.9 gm. Hg.), of which there were in the feces 95 per cent., or 2.1175 gm.; in the urine, 0.055; in the brain, heart, lungs, spleen, pancreas, kidneys, scrotum, and penis, 0.009; in the liver, 0.014; in the muscles, 0.0114. If the poison find access to the body by external appli-

cation or by irrigation of other cavities than the alimentary tract, it should be looked for in the liver, the urine, and the kidneys. Other cases have been reported which established the fact that in a few days the whole amount of one poisonous dose given by the mouth may escape from the body.

There is liability to error if the analyst loses sight of the well-known fact that traces of mercury are very commonly found in the stomach, bowels, liver, kidneys, and other organs of the cadaver with no history of recent dosage from the poison. These are probably accumulations from small non-poisonous doses of blue mass or calomel, or perhaps vestiges of a previous mercurial treatment of syphilis.

Detection.—A ready, casual examination can be made of the vomited matters or urine by decanting the liquid portion, evaporating it to dryness, treating with pure hydrochloric acid, and applying Reinsch's test, the galvanic gold test, or the electrolytic test.

Separation from the tissues or other organic matter is accomplished by the systematic method referred to under Arsenic. To disintegrate the organic matter thoroughly it must be finely minced and heated on a water-bath for some time with equal parts of water and hydrochloric acid, while potassium chlorate is added in small amounts until a clear solution is made. After filtration the solution is heated gently to expel the chlorin and a stream of hydrogen sulphid is passed until the metal is all precipitated as sulphid. A portion of this sulphid may be tested by reduction and sublimation, or it may be dissolved by gentle heat in nitrohydrochloric acid, the solution evaporated to dryness on a water-bath, redissolved in warm water, and the above tests be applied or the mercury separated by electrolysis.

Electrolysis may be performed conveniently by the method of Mann. The suspected solution is put in a glass cell having a bottom of parchment-paper, and immersed to a common level in an outer vessel of water acidulated with sulphuric acid. The cathode of a battery of four Grove cells, made of a slip of gold-foil, is fixed into the inner vessel near to and parallel with the bottom. In the outer liquid is set the anode, a strip of platinum opposite to the cathode. After the current has passed six hours, the gold coated with mercury is washed successively with water, alcohol, and ether, and weighed. By heating the gold-foil in a hard glass open tube of known weight the mercury sublimes and is deposited on the tube.

Quantitative determination may be made by finding the loss of weight of the gold-foil carrying a film of mercury when heated as above described. This gives the weight of mercury in the

portion of fluid tested; it can be controlled by calculating the increase of weight in the tube. Instead of using electrolysis, the amount of corrosive chlorid present in any fluid in which mercury is sought may be determined simply by boiling the materials in water, straining, filtering, and agitation of the filtrate with ether, separation, and evaporation of the ethereal extract. The dried residue dissolved in water may be precipitated with volumetric solution of silver nitrate, the chlorin estimated, and from this the weight of mercuric chlorid calculated.

Urine examination may be made by electrolysis, Reinsch's test, or by Mayer's method, which follows: Having evaporated the urine to dryness, the residue, mixed with quicklime and slaked lime, is heated in a combustion tube, condensing the mercury on the cooler part.

Rapid Method.—Separate the mercury from organic combinations by heating to the boiling-point in a porcelain dish a mixture of 20 fl. oz. (600 c.c.) of urine with 4 fl. oz. (100 c.c.) of hydrochloric acid and 7 gr. (0.50 gm.) of potassium chlorate. Before it has cooled it is poured through a filter (if turbid) into a funnel having a stopcock, previously adjusted to permit 100 c.c. to pass in one minute. The end of the funnel rests in a smaller funnel-tube, the outlet of which has been heated and drawn into a fine opening. Inside this narrowed tube has been placed a small spiral of bright copper-foil. Having passed all the urine through the funnels and over the copper, the operation is repeated six times, keeping the urine hot. If mercury be deposited, the copper will change color. The copper spiral is taken out with forceps, washed in water, alcohol, and ether, dried, and heated in a narrow tube. The mercury vaporizes and is condensed as globules on the glass.

LEAD (Plumbum)

Symbol, Pb. Atomic weight, 207.1.

There are numerous compounds of lead in nature, the most important being *galena*, the sulphid, PbS. This is roasted till oxidized and the oxid is reduced with carbon.

Properties.—Lead is a soft bluish-white metal, heavy, but of low melting-point, 325° C. (617° F.). Freshly cut surfaces have a brilliant luster which is soon lost, a superficial layer of oxid being deposited by the action of the air. The softness, pliability, and low melting-point of lead make it a convenient material for plumber's pipe. *Soft solder* is an alloy of lead and tin. *Type metal* contains lead, tin, and antimony. *Pewter* contains lead and tin. Metallic lead dissolves freely in nitric acid, sparingly in strong sulphuric acid when hot, but not in dilute or cold sulphuric acid,

nor practically in hydrochloric acid. The metal, when embedded in the tissues as a bullet, exerts no local specific action, being insoluble in the fluids there. While not soluble in pure water, the ordinary water served in plumber's pipes contains enough free oxygen to oxidize a fresh lead surface, which may then form a soluble bicarbonate by the aid of the carbon dioxid present. A portion of it finally forms a crust of insoluble hydrated oxycarbonate, which prevents further action. While silicates, sulphates, and carbonates tend to prevent the corrosive action of water, it is increased by nitrites, nitrates, and chlorids. Hence, a *hard* water supply is less dangerous when served in lead pipes than a "soft" or purer article.

The Ions of Lead.—The element itself forms a bivalent cation, Pb^{++}, called *plumbion*, and an unstable quadrivalent, cation,—Pb^{++++}. Plumbion is without color and is a potent poison. When lead is acted upon by air and water a white precipitate of lead hydroxid, $Pb(OH)_2$, forms which behaves toward alkalis just as does alumina—that is, it dissolves in excess of alkali, but not in ammonia. With those bases it forms soluble *plumbites*, the hydroxid having split off hydrogen to form complex anions, such as $(PbO_2)^=$ and $(HPbO_2)^-$. A hypothetic hydroxid, $Pb(OH)_4$, is supposed to contain the quadrivalent anion $(PbO_4)^{\equiv}$, and has received the name of *normal plumbic acid*. This, by the loss of water, forms *metaplumbic acid*, H_2PbO_3. With calcium the former makes *calcium plumbate*, Ca_2PbO_4; with sodium the latter makes *sodium metaplumbate*, Na_2PbO_3. These acids combine with lead itself to make Pb_2PbO_4 or Pb_3O_4, *minium*, and $PbPbO_3$ or Pb_2O_3, the *sesquioxid*.

Lead Oxid (PbO) (*Plumbi Oxidum, Litharge*).—When air or oxygen is caused to pass over salts of lead, heated or melted lead, a yellow powder forms. This powder, fused at a higher temperature, forms yellowish crystalline scales of PbO called commercially *litharge*. Continued gentle heat in air changes it to a bright-red powder, Pb_3O_4, used as a pigment under the names *red lead*, or *minium*. If the red lead be oxidized by heating with nitric acid, a dark-brown powder forms, the *dioxid* or *peroxid*, PbO_2. The oxid, PbO, dissolves sparingly in water, imparting an alkaline reaction, due to the formation of lead hydroxid, $Pb(OH)_2$. It is strongly basic, decomposing alkaline salts. With the fatty acids of oils it unites to form lead soaps, the most important of which is lead oleate or *emplastrum plumbi*. Heated with milk of lime its hydroxid develops acid properties as H_2PbO_2, forming a soluble crystalline *calcium plumbite*, $CaPbO_2$, used as a hair dye.

Lead dioxid (PbO_2) (*peroxid, brown oxid, puce oxid*) is an

insoluble dark brown powder, readily yielding half its oxygen when heated. It is much used in the laboratory as an oxidizing reagent.

Lead chlorid, $PbCl_2$, is formed by a reaction between a soluble lead salt and a chlorid; or whenever plumbion and chloridion are brought together in concentrated solution. It is a white crystal, very sparingly soluble. Uniting with lead oxid it forms several basic or oxychlorids of a yellow color, which are used as pigments under the names of *Turner's*, *Naples*, *Verona*, or *Paris yellow*.

Lead nitrate, $Pb(NO_3)_2$, is prepared by dissolving lead or lead oxid in dilute nitric acid. While readily soluble in water it is very sparingly soluble in strong nitric acid. It is white and sweetish, the after-taste being metallic and astringent.

Lead sulphate, $PbSO_4$, is formed when hot strong sulphuric acid acts on lead. It is the heavy white precipitate that falls when plumbion, Pb^{++}, meets sulphanion, $(SO_4)^=$, as happens when sodium or magnesium sulphate is given as an antidote to lead-poisoning, thus:

$$Pb^{++}, (NO_3)^-, (NO_3)^- \quad + \quad K^+, K^+, (SO_4)^= \quad =$$
$$K^+, (NO_3)^- \quad + \quad K^+, (NO_3)^- \quad + \quad PbSO_4.$$

It is sometimes used to give weight or body to white silk, and from this fabric it may be taken accidentally by seamstresses.

The *storage battery* or *accumulator* contains a plate of lead and one of lead dioxid, PbO_2, immersed in sulphuric acid. A *charging* electric current, having been sent through the cell, has accumulated as intrinsic or chemical energy in the Pb^{++++}, $O_2^=$. When the circuit is closed this stored energy flows back as a discharging electric current, while the two plates are both converted to lead sulphate. The quadrivalent Pb^{++++} in the PbO_2 gives up two charges of electricity to become the Pb^{++} in $PbSO_4$. The battery is restored by a charging current which reverses the reaction, raising the Pb^{++} to its former state of Pb^{++++}.

Lead Carbonate ($2(PbCO_3) . Pb(OH)_2$) (*Plumbi Carbonas, White Lead*).—The paint known variously as *white lead*, *flake white*, and *mineral white* is a mixture of lead hydroxid and neutral lead carbonate. It is present in the official ointment of lead carbonate. It is the white precipitate formed when plumbion, Pb^{++}, and carbanion, $(CO_3)^=$, meet in the same solution. To facilitate the reaction between lead oxid and carbon dioxid the vapor of acetic acid is used as an intermediary. First a basic acetate is formed, and this changes to the basic carbonate. It is a smooth, white, insoluble, tasteless powder, invaluable as a base for paints. Sometimes it has been used

as a cosmetic with the most deplorable consequences. It is the most common cause of chronic lead-poisoning.

Lead chromate, $PbCrO_4$, is the heavy yellow precipitate formed when plumbion, Pb^{++}, meets chromanion $(CrO_4)^{=}$.

$$Pb^{++}, (NO_3)^-, (NO_3)^- \quad + \quad K^+, K^+, (CrO_4)^{=} \quad =$$
$$K^+, (NO_3)^- \quad + \quad K^+, (NO_3)^- \quad + \quad PbCrO_4.$$

It is an amorphous, insoluble powder used as a pigment under the name *chrome yellow*. The basic chromate is known as *chrome orange*.

Lead acetate, $Pb(C_2H_3O_2)_2 3H_2O$, *plumbi acetas*, is made by the action of acetic acid on lead oxid. It occurs in white masses of acicular crystals. It is soluble in water, and has a taste at first sweetish, hence the popular name, *sugar of lead*, but later the taste is styptic and metallic in character. It is present in pharmaceutic preparations, as a pill, with opium, a compound suppository with opium, and an ointment. The subacetate, $Pb(C_2H_3O_2)_2PbO$, made by dissolving the oxid in solutions of the acetate, is present (25 per cent.) in *liquor plumbi subacetatis*, "Goulard's Extract;" in a dilute form (1 per cent.) in *liquor plumbi subacetatis dilutus* (lead-water), and in *ceratum plumbi subacetatis* (all U. S. P.). Clear solutions soon turn white from the action of carbon dioxid in the air. This tendency is arrested by adding acetic acid in excess. This property is not shared by the solution of the nitrate, which keeps clear.

Toxicology of Lead Salts.—In spite of its great frequency, lead-poisoning rarely figures in the courts, owing to the fact that most of the cases are due to slow absorption of minute quantities, exposure to which is an incident of certain industries dealing with lead or its compounds. The fatal cases represent but a small fraction of the persons who, from numberless causes, suffer from degrees of chronic poisoning more or less serious, but not ending in death.

Poisonous Salts.—The salt which is of most importance in acute poisoning is lead acetate, while chronic poisoning is most frequently caused by lead carbonate.

The subacetate of lead present in Goulard's extract has very much the same effect as the acetate, but greater in degree, as it contains more lead. Lead chromate (chrome yellow), lead oxids (litharge and red lead), and finely divided metallic lead, while not soluble in pure water, dissolve in certain natural waters containing nitrates and nitrites and in the dilute vegetable acids of food and in the gastric juice, are absorbed in the intestines, deposited in various tissues, and exert a slowly cumulative poisonous action.

Ledoyen's Disinfectant," containing lead nitrate, and "Turner's yellow," or the oxychlorid—in fact, all the salts of lead are poisonous, except perhaps the sulphid and sulphocyanate.

Acute Lead-poisoning.—*Symptoms.*—At first they are such as result from a local irritant, and are less likely to be fatal from a single large dose than from the same amount taken in fractions at intervals. In a few minutes a metallic taste is perceived, and soon afterward the mouth and throat feel dry and burn. Retching and vomiting may appear in less than half an hour and prove obstinate and persistent. Abdominal pains come on in colicky cramps, relieved by pressure. Usually the bowels are constipated; occasionally the stools are bloody, and at a later date they are dark from lead sulphid. The urine is scanty, the face anxious, the skin dry, the breath fetid, and the tongue coated. While the brain is clear, the involvement of the nervous system is indicated by the headache, the pain and cramps in the legs, and the numbness and local palsies which appear a few hours later. After a few days in some cases a blue line is seen on the gums.

Fatal Dose.—It is not known what single dose of lead acetate would prove fatal. Since recovery has taken place in 3 cases after taking 1 oz. (28.3 gm.) of the acetate, it would seem that the fatal amount must be greater when that salt is the poison. It is probable that the fatal dose of the carbonate would be somewhat less than that of the acetate, though the course of the symptoms would be slower.

Fatal Period.—While death from the acute form is very rare, 23 cases have been collected. It may occur from prostration as early as the second or third day.

Treatment.—The first indication is the washing-out of the stomach by a tube or pump, using a solution of sulphates of magnesium or sodium. In the absence of the tube an emetic dose of alum (a soluble sulphate) would be serviceable. When the stomach is quiet, the remainder of the poison can be neutralized and the bowels evacuated by $\frac{1}{2}$ oz. of magnesium sulphate (Epsom salt). To check vomiting and colic the best reliance is on hypodermic injections of morphin and atropin.

Postmortem Appearances.—In the few autopsies which have been held in acute lead-poisoning indications have been found of gastro-intestinal inflammation. When life has been prolonged until systemic symptoms appear, lesions have been found in the liver and kidneys.

Chronic Lead-poisoning (*Plumbism, Saturnine Intoxication*).—Judging by the cases reported in the medical journals, chronic poisoning is of very common occurrence. In the vast majority the lead enters the body by accident, as a result of its use in cer-

tain industries; in a certain proportion it is caused by contamination of food and drink. In these cases the amount of lead in each dose is so small as to escape detection, but, owing to its extraordinary cumulative action, in time a sufficient quantity finds lodgment in different organs to produce widespread damage.

Injurious Industries.—Operatives in the *metal* are liable to have it introduced by inhalation, by dust particles getting in the hair, beard, or clothing, and indirectly into food and drink, and possibly through the skin. In this way many cases have been caused in plumbers, smelters, type-founders, compositors, shot-makers, file-cutters, lead-foil workers, etc. It is even more common in those who work in the lead salts used for colors, such as color-grinders, white- and red-lead makers, japanners, enamelers, lapidaries, potters, combers of yarn dyed with chrome yellow, and workers on the lead plates of electric accumulators.

Food Contamination.—As lead is slightly soluble in water containing certain salts and gases (see p. 323), its widespread use for pipes in which beverages are kept standing over night causes it to be introduced into drinking water, into ale and beer drawn from the cellar, and into seltzer-water kept in siphons. Lead oxid is largely used to make a glaze on pottery. From this it may be dissolved by acid foods, as fruit jellies, pickles, vinegar, and lemon-juice. As a constituent of solder and the alloy used to tin iron it finds access to canned goods containing acids.

As a substitute for the yellow of egg in making sweet cakes, lead chromate, $PbCrO_4$, under the name "*chrome yellow*," has been used by bakers, with very grave consequences. An epidemic of lead-poisoning in the north of France, involving over 100 persons, was traced to lead in the flour which was obtained by all the sufferers from the same mill, contamination being due to the elevator buckets, which were "tinned" with lead.

Cosmetics.—Most of the lotions called "hair-renewers" are preparations containing sulphur with lead acetate or calcium plumbite. They do not restore the natural pigment, but cause the precipitation of black lead sulphid in the hair structure, so as to simulate the natural color. The use of "flake white" as a cosmetic has caused every form of chronic lead-poisoning.

Symptoms of Chronic Lead-poisoning.—In this condition there are emaciation, a feeling of "poor health," feeble appetite, impaired digestion, weakened energies, low spirits, and more or less profound anemia, as shown by the pallor. The most characteristic symptoms are weakness of the forearms with dropping of the wrists ("the dangles"); colic with constipation ("dry belly-ache"); a blue line on the gums and blue patches on the cheeks opposite; headaches; joint pains which may be mistaken for rheumatism or

gout; melancholia or mania; convulsions, sometimes classed as epileptic. Albumin in the urine points to the kidneys as the seat of serious chronic disease caused by the lead. The blue line on the gums is caused by the reaction between lead chlorid in the gum and hydrogen sulphid of decomposed food particles between the teeth. The formation of the black sulphid is explained by this equation:

$$PbCl_2 + H_2S = 2HCl + PbS.$$

The black deposit seen through the opalescent mucous membrane has a bluish color. Lead is found in the urine of most cases examined.

The fatal cases are characterized by convulsions due to brain disease. It has been suggested that the gravity of the nervous phenomena in poisoning from lead chromate is due in some degree to the chromium present in the poison.

Lead appears to form some stable combination with the substance of the nervous system, and induces thereby disturbed function, if not local destruction, of some essential part of the great centers, as well as of the peripheral nerves. In a case of fatal lead-poisoning the cerebrum was found to contain lead equivalent to $1\frac{1}{2}$ gr. of sulphate and the cerebellum about $\frac{1}{4}$ gr. An optical neuritis may cause visual disturbances, but these are sometimes due to the retinitis secondary to the kidney mischief.

Treatment of Chronic Poisoning.—By careful inquiry the source of the lead may be discovered, and the patient should be guarded against further exposure to it. In the case of operatives in lead-works, emphasis must be laid upon the necessity of grinding the pigments under water to prevent the fine particles escaping as dust into the air; free ventilation is requisite; the hands, nails, and beard should be washed and brushed carefully before eating, and meals should not be taken inside the factory. A weak lemonade of sulphuric acid is sometimes used as a beverage. Its antidotal power may be reinforced by occasional doses of magnesium sulphate.

It is well to begin treatment with some magnesium sulphate as an antidote to any lead present in the alimentary tract; colic will call for morphin and atropin administered hypodermically; joint-pains for local fomentations; paralysis for electricity and massage. The natural process of elimination of lead is deliberate. It escapes slowly by the urine, and five to ten times as much by the bowels, without the use of any special eliminant. Several special eliminants, notably potassium iodid, have been given freely without causing any increase in the amount of lead excreted.

Careful quantitative tests prove that a slight increase attends the use of hot baths, general massage, and occasional purgation. These last, combined with open-air exercise and wholesome diet, are the means most to be relied on. If potassium iodid is given, care should be taken that it does not increase the anemia. A remission should be allowed, during which iron preparations would be of service.

Postmortem Appearances.—In chronic cases the pathologic changes discovered cannot be called characteristic. Where albuminuria has been present, the kidneys are found hard and contracted, the seat of granular degeneration. When colic has been a conspicuous symptom a portion of the intestines has been found constricted, with a gray-black discoloration of the mucous lining. When there has been local paralysis with atrophy the muscles involved have been found wasted and fatty, and changes have been discovered in the large cells in the anterior cornua of the cord and in the peripheral nerve-fibers. The blue line around the gums is highly significant.

Distribution in the Tissues.—In examining the bodies of 2 cases suddenly fatal, Blyth separated from the brain of one an appreciable amount of lead, from the liver an amount equivalent to $\frac{1}{3}$ gr. of sulphate, from one kidney about $\frac{1}{13}$ gr. In a dog killed by chronic lead-poisoning, in parts per thousand, the bones were found to contain 0.18 to 0.27; the kidneys, 0.17 to 0.20; liver, 0.10 to 0.33; spinal cord, 0.06 to 0.11; brain, 0.04 to 0.05; muscles, 0.02 to 0.04; intestines, 0.01 to 0.02, and traces were detected in the spleen, blood, and bile.

It is a remarkable fact that lead is frequently found in the cadavers of persons who in life were free from all symptoms of lead-poisoning. A fallacious conclusion may be reached if the contents of the stomach should contain a bit of melted solder from a fruit can or a shot derived from eating game.

In the absence of characteristic symptoms during life, if the amount of lead separated from the tissues should be small, it should not be regarded as significant of lead-poisoning.

Lead in the Urine.—From a case which had symptoms so vague as to make the diagnosis of lead-poisoning doubtful there was obtained from 400 c.c. (14 fl. oz.) of urine as much as 5.2 mg. (0.08 gr.) of metallic lead. Elimination is not always uniform. For a long time the urine is free from lead and later shows it, without further administration in the meantime.

There is reason to believe that lead is not an uncommon constituent of the urine. Urine analyses for lead were made in 86 cases, in the healthy and the sick, with the result of finding lead present in 48 cases. Most of them were chosen because of their

exposure to lead by occupation or otherwise, and, so far as these figures are a guide, in not more than 50 per cent. of the community at large can lead be detected in the urine. The urines of persons known to be in perfect health were almost all free from lead.

Tests.—Hydrogen Sulphid.—A stream of this gas passed through a lead solution, neutral, alkaline, or slightly acid, yields a black precipitate of lead sulphid, insoluble in the alkaline hydroxids or the moderately dilute acids. If the amount of metal be very small, the precipitate will be brown. Hot nitric acid converts it into soluble lead nitrate and free sulphur separates; by continued heat the acid converts the sulphur into sulphuric acid, and this precipitates the lead as lead sulphate. A small amount of lead would remain in solution.

Fallacies.—This reagent gives a like precipitate with several other metals, such as copper and mercury. To distinguish the lead the sulphid may be dissolved in warm dilute nitric acid, filtered, the filtrate evaporated to dryness to expel any excess of nitric acid, the residue taken up with water, and the clear solution tested, as stated below, with potassium iodid, dilute sulphuric acid, or potassium chromate. If the quantity of the precipitate be large, it can be reduced to metallic lead by the blowpipe or charcoal.

Delicacy.—From a solution containing $\frac{1}{25000}$ gr. of lead oxid to 10 gr. of water this test gives a faint brownish tint with perceptible cloudiness.

Potassium Iodid.—This reagent gives, with very small amounts of lead, a yellow coloration; with larger amounts, a yellow precipitate of lead iodid, soluble in boiling water, from which it deposits, on cooling, in gold-colored hexagonal scales.

Fallacies.—If the lead be small in amount and has been treated previously with nitric acid, a brownish color will be caused by the iodin freed from the potassium, unless the free nitric acid has been neutralized or driven off by heat. Lead iodid is soluble in potassium hydroxid and in strong hydrochloric acid.

Delicacy.—A very small quantity of the reagent will cause a satisfactory deposit of small plates from a solution of $\frac{1}{20000}$ gr.

Sulphuric Acid.—This reagent, diluted, gives a white crystalline or granular precipitate of lead sulphate, which is favored by the addition of alcohol. The precipitate is soluble in hot strong hydrochloric acid, in ammonium acetate, and in a large excess of potassium hydroxid.

Fallacies.—This reagent will also make a white precipitate with barium and strontium salts, and with fairly strong solutions of calcium compounds. The lead sulphate is characterized, however, by turning black with ammonium sulphid.

Potassium Chromate or Dichromate.—Either of these reagents precipitates lead as a yellow amorphous deposit soluble in potassium hydroxid and strong hyrochloric acid, but insoluble in acetic acid. A yellowish precipitate produced by potassium chromate in neutral copper solutions dissolves in acetic acid and is thus readily distinguished from the lead precipitate.

Detection in Gastric Contents, Tissues, etc.—A method suitable for the urine, feces, gastric contents, or the finely divided viscera is the evaporation of the fluid or the dilution of the solids to the consistence of a gruel, the destruction of organic matter with potassium chlorate and hydrochloric acid (see p. 283), and filtration while hot. While some of the lead is apt to remain as insoluble sulphate on the filter, a considerable quantity in a soluble combination with potassium chlorid passes through. In toxicologic analysis, as a rule, the total amount of lead is not in excess of what will be dissolved. The filtrate may be precipitated with hydrogen sulphid, the precipitate dissolved in warm dilute nitric acid, the solution filtered and evaporated to dryness, the residue redissolved in water, and tested with sulphuric acid or potassium iodid.

Detection in Urine.—The following method for the urine is very delicate: A quart of urine acidified with acetic acid is evaporated to dryness and fused in a crucible with a little pure niter until it becomes white. When the crucible is cool, dilute hydrochloric acid is added *hot* to extract the residue after ignition. The extract is then filtered, and the filtrate treated with ammonium to alkaline reaction, to precipitate the phosphates and iron. Ammonium sulphid is added at the same time to throw down the lead and iron as sulphids. This deposit is washed three times by decantation with hot water; then water acidified with hydrochloric acid is added, and the whole allowed to stand until the next day. It is then filtered through a small filter and the residue washed. A little pure nitric acid is then added, drop by drop, to dissolve the lead sulphid left on the filter and carry it through as nitrate. This filtrate is collected in a watch-glass, evaporated to dryness, and the final test made by adding a drop of water and a crystal of potassium iodid. A yellow precipitate denotes lead.

Electrolysis.—To electrolyze the filtrate of the hot decoction with potassium chlorate and hydrochloric acid it is placed in a glass vessel with a bottom of parchment-paper. This cell is immersed to the surface level in an outer vessel containing distilled water acidulated with sulphuric acid. In the inner cell is placed the cathode of four Grove cells in the shape of platinum foil 50 cm. square (2 in. by 4 in.). Beneath the parchment diaphragm, near to it and parallel with the cathode on the opposite side, is

placed the anode. In six hours the cathode is removed, washed, dried, and cleaned of its lead with warm dilute nitric acid. After driving off the free nitric acid by heat the lead is precipitated by dilute sulphuric acid and an equal volume of alcohol added. After being set aside for twenty hours the precipitate is washed free from acid with water containing 12 per cent. of alcohol. Decanted, ignited, and weighed, 100 parts of the sulphate equal 68.319 parts of metallic lead.

Quantitative Determination.—While the electrolytic method is preferable when the amount of lead is small, for large quantities it is better to precipitate the lead dissolved by decoction in hot hydrochloric acid with hydrogen sulphid. The precipitate may be converted into sulphate by treating it first with warm dilute nitric acid, filtrating, evaporating, dissolving in water, and precipitating with sulphuric acid, evaporating, igniting, and weighing as above, calculating 68.319 parts of lead for 100 of the sulphate.

BISMUTH

Symbol, Bi. Atomic weight, 208.

Occurrence.—The metal occurs free in nature and also as a sulphid. From this sulphid it is obtained by first roasting until it is converted to oxid, and then reducing the oxid with carbon.

Properties.—Bismuth is a reddish-white, brittle, crystalline metal. Its crystals are isomorphous with arsenic and antimony. It is unchanged by air or water, and is a good conductor of electricity. Its ion is the trivalent bismuthion, $Bi^{\cdot\cdot\cdot}$. It forms some alloys that melt below the boiling-point of water.

Rose's fusible metal consists of bismuth 2 parts, lead 1, and tin 1. It melts at 93.8° C. (201° F.).

Wood's metal consists of bismuth 4 parts, lead 2, tin 1, and cadmium 1. It melts at 60.5° C. (141° F.).

Bismuth sesquioxid, Bi_2O_3, is a yellow powder formed by burning bismuth in air. It is also formed when the hydroxid, $Bi(OH)_3$, is heated and loses water. Both are basic.

Bismuth hydroxid, $Bi(OH)_3$, is precipitated from bismuth solutions by excess of alkali. It is an insoluble white powder. With nitric acid it forms *bismuth nitrate,* $Bi(NO_3)_3$, showing that it is a triacid base. By losing the constituents of water, $Bi(OH)_3$ changes to *bismuthyl hydroxid,* BiO.OH, which is a monacid base. In reacting with nitric acid the hydroxyl is replaced and *bismuth oxynitrate* or *subnitrate,* $BiO.NO_3$, is produced. A whole series of subsalts or basic salts are formed by this univalent group, *bismuthyl,* BiO.

Bismuth Subcarbonate [$(BiO)_2CO_3.H_2O$] (*Bismuthyl Carbonate*

Oxycarbonate).—This is formed when a solution of the normal nitrate is treated with sodium carbonate. Carbon dioxid is given off, and the subcarbonate is precipitated as a yellowish-white insoluble powder. When heated, water and carbon dioxid escape, leaving bismuth oxid, Bi_2O_3.

Dose: 10 to 60 gr. (0.666–4 gm.).

Bismuth Subnitrate ($BiO.NO_3.H_2O$) (*Bismuthyl Nitrate, Oxy-nitrate*).—When bismuth is dissolved in nitric acid a clear solution of the normal nitrate, $Bi(NO_3)_3$, is obtained. By pouring this solution into water a heavy white precipitate of bismuthyl nitrate forms, and some nitric acid is left, possibly in combination with bismuth:

$$Bi(NO_3)_3 + 2H_2O = BiONO_3.H_2O + 2HNO_3.$$

Dose: 10 to 60 gr. (0.666–4 gm.).

Incompatibles.—Tannic and gallic acids; calomel; sulphur; salicylic acid; potassium iodid; with alkaline bicarbonates it causes effervescence.

Nylander's reagent is an alkaline solution of bismuth hydroxid by means of sodium potassium tartrate (p. 621). When boiled with a glucose solution the reduced metal bismuth is precipitated gray or black.

Bismuthi et ammonii citras (U. S. P.) is of indefinite composition. The ordinary citrate of bismuth, $BiC_6H_5O_7$, is a white insoluble powder which in ammonium hydroxid becomes soluble. This double citrate forms small pearly scales which are soluble in water. Dilute acids change it to the insoluble form. Dose: 1 to 5 gr. (0.066–0.33 gm.).

Other official compounds of bismuth are *Bismuthi citras*, dose, 2 gr. (0.125 gm.); *bismuthi subgallas*, dose 4 gr. (0.250 gm.) and *bismuthi subsalicylas*, dose 4 gr. (0.250 gm.).

Toxicology.—The study of the toxic action of bismuth is practically that of the salt most commonly used in medicine, the *subnitrate*. This white, odorless, almost tasteless, and nearly insoluble powder, is sometimes used as a cosmetic under the name of "pearl white." It is much esteemed as a local sedative for gastric and intestinal irritation and is given almost *ad libitum*. At one time most samples were imperfectly freed from the arsenic which is found associated with bismuth in its ores. Antimony, lead, and a trace of tellurium have been found in it. At present, contaminants are rarely detected, owing to the more perfect methods of preparation now employed. Owing to its difficult solubility, the pure subnitrate in any but very large doses has no toxic action. When applied to open wounds and extensive burns

as an antiseptic, some absorption is apt to occur with symptoms of systemic poisoning.

Symptoms.—While the salt itself has only a feebly acid taste, yet in cases of poisoning from absorption a peculiar metallic taste is complained of, accompanied by salivation, foul breath, and sore mouth. There are vomiting, abdominal pain, and purging of stools, dark from bismuth sulphid. Sometimes a black discoloration appears upon the gums, but may spread over the whole mouth. The reaction of the hydrogen sulphid generated from decomposed food with bismuth subnitrate is as follows:

$$2BiONO_3 + 3H_2S = Bi_2S_3 + 2HNO_3 + 2H_2O.$$

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The black Bi_2S_3 is insoluble in ammonium sulphid, which thus separates it from the sulphids of arsenic and antimony.

The strong garlicky odor of the breath sometimes observed has been attributed to tellurium, which produces this effect, although the amount is very minute. As the gastro-enteric symptoms are similar to those of arsenic, the toxic action of bismuth was at one time ascribed to that impurity. Large doses internally, as well as free topical applications of bismuth salts, have in some cases caused black urinary sediment, albuminuria, and tube-casts, beside the usual stomatitis, loosened teeth, blue gingival line, diarrhea, and ulceration of the intestines.

Cases have been described which show peculiar effects on the mouth when the bismuth salt has been absorbed at distant points, due to the fact that bismuth is eliminated largely by the saliva. These cases are remarkable because equally large amounts have been administered by the mouth without injurious consequences. In one case an extensive burn was treated with local applications of bismuth subnitrate, proved by analysis to be pure. In two weeks there was a severe inflammation of the mouth and throat with adherent black exudations; vomiting and diarrhea supervened with albuminuria. Bismuth was detected in the urine and the feces. A few days after the application was discontinued the acute symptoms subsided.

An experimental research on the lower animals, using a pure salt of bismuth hypodermically, caused death after symptoms like those just described.

Fatal Dose.—The earlier reports as to the fatal dose must be taken with much allowance, owing to the fact that until recent times the bismuth salts almost always contained enough arsenic to cause trouble if the dose was a liberal one. Death has followed a dose of 2 dr. The period of fatality was the ninth day. A dose three times as large has been recovered from.

Tests.—Hydrogen sulphid yields a black precipitate of bismuth sulphid. If this is dissolved in the smallest possible quantity of hot nitrohydrochloric acid and the resulting solution poured into an excess of water, a copious white precipitate of bismuth oxychlorid is thrown down.

Extraction from the tissues is done by boiling the finely divided matter for two hours in dilute nitric acid, the dissolved material separated by filtration, and the filtrate evaporated to dryness. The undissolved organic matter is destroyed with strong nitric acid and then boiled with dilute nitric acid, filtered, and dried.

A solution of both residues is made in 50 per cent. nitric acid and the above tests are applied.

SILVER (Argentum)

Symbol, Ag. Atomic weight, 107.88.

Occurrence.—Metallic silver is sometimes found free in nature. Its chief ore is a sulphid which also contains lead sulphid. Lead and silver are extracted together and roasted in air. The lead oxidizes to litharge, but silver retains its metallic character, even at a high heat, like the other *noble* metals.

Properties.—Silver is tenacious, pure white in color, and maintains the highest luster, resisting perfectly the action of oxygen and water vapor. By air containing a trace of hydrogen sulphid and by other sulphids and organic-sulphur compounds, silver is blackened with a film of sulphid. It has a specific gravity of 10.5, is the best conductor of electricity and heat, and melts at 1000° C. (1832° F.). When the metal is precipitated in the metallic state by reduction from the solutions of its salts, it is not white, like the normal form, but may be yellow, brown, gray, or black. When reduced from alkaline solutions it assumes a suspended condition of a red or brown color; and when dry takes on a metallic luster and any one of several colors—yellow, green, red, or violet. These are considered to be allotropic forms.

Colloidal Silver.—In the presence of organic compounds like gelatin, casein, citric acid, etc., reducing agents act without precipitation. The result is an olive-brown, stable solution which should not be exposed to light or air. This colloidal silver differs from metallic silver in being apparently soluble in water, yet it dissociates very little *argention* for the reaction with chloridion. Though it is bactericidal and used as a surgical antiseptic, it does not permeate membranes. The only difference between this colloidal solution and a true suspension is that of size of the sus-

pended particles. Those of the colloidal solution are so small that by collisions with each other they keep suspended and overcome the gravitation tendency. The *ultramicroscope*, by intense oblique illumination, makes the particles visible like those of dust floating in the air when illuminated by a sunbeam.

By its luster and rarity silver commends itself for precious coins, but because of its softness it is not fit for any rough use until alloyed with about 10 per cent. of copper, which makes it harder. From coins pure silver is obtained by first dissolving in nitric acid, which takes up both silver and copper and precipitates the silver with sodium chlorid, leaving the copper nitrate in solution. Silver chlorid, dried and heated in a crucible with sodium carbonate, yields the silver as a metallic button, the chlorin going to the sodium to form sodium chlorid and carbon dioxid escaping as vapor.

Silver is not affected by the strongest alkalis, nor by any dilute acid except nitric. It is soluble in nitric and sulphuric acids and solutions of potassium cyanid.

The Ion of Silver.—Argention, $Ag^{\cdot}$, is univalent and colorless. Its hydroxid is strongly basic, like the alkalis, forming soluble salts that are neutral. The ion passes into the metallic state with great readiness. Its salts in contact with organic matter, stimulated by sunlight, separate the finely divided metal of a brown or black color. Metallic silver is not poisonous, as is often demonstrated by the use of silver wire in closing wounds by suture, and the absence of injurious consequences when silver coins have been swallowed accidentally. But argention is an active poison. It is, however, a reagent for precipitating halogens, and, owing to the wide distribution of the chloridion of common salt in the tissues, the argention is quickly thrown out of action and then reduced to the metallic state as a permanent deposit.

Silver Oxid (Ag_2O) (*Argenti Oxidum*).—There are three oxids of silver: Ag_4O, AgO, and Ag_2O. The last is called *normal*, and is the only one of medical interest. At ordinary temperature the alkaline hydroxids precipitate from solution of silver nitrate this normal silver oxid, Ag_2O. It is a brown powder of slight solubility, but sufficient to give an alkaline reaction. Dose: $\frac{1}{6}$ to $\frac{1}{4}$ gr. (0.011–0.016 gm.), best mixed with chalk and given in capsules. It is *incompatible* with ammonia, phosphorus, organic matter, and the salts of mercury, iron, bismuth, and copper.

Silver Chlorid ($AgCl$) (*Argenti Chloridum*).—This is the white precipitate formed when the ions of silver and chlorin meet. A white powder, it turns gray and violet on exposure to light, the darkening being due to change of $AgCl$ to the subchlorid, Ag_2Cl, and free chlorin; it is in proportion to the intensity of the

light. While very sparingly soluble in water silver chlorid dissolves in ammonia, the thiosulphates, and potassium cyanid.

Silver bromid, $AgBr$, is obtained as a fine yellowish precipitate when argention and bromidion are brought together. It resembles silver chlorid, but is much less soluble in ammonia, though soluble in thiosulphates. It is more sensitive to light than the chlorid.

Bromid-gelatin plates for photography are prepared by adding ammonium bromid to solution of gelatin, and in the dark adding silver nitrate. Silver bromid is precipitated in a finely divided state, embedded in the gelatin:

$$AgNO_3 + NH_4Br = NH_4NO_3 + AgBr.$$

By washing the cooled mass the excess of ammonium bromid and the ammonium nitrate are removed. When warmed, the *sensitive gelatin* melts and is applied as a thin film to glass or celluloid. Such a plate in the focus of a camera has its silver bromid reduced to sub-bromid in proportion to the light coming from the object.

Developers.—The process of reduction is completed by immersing the plate in a reducing liquid called a *developer.* The developer is a solution of ferrous sulphate, pyrogallic acid, potassium ferro-oxalate, etc. Metallic silver is deposited in proportion to the intensity of the light that made the initial reduction. The lights of the picture have caused a dense precipitate, the shadows little or none. At a satisfactory point in development the plate is washed free of silver bromid by sodium thiosulphate, or *hypo*, and there remains a fixed *negative*—that is, a picture which reverses the lights and shadows.

Silver Nitrate ($AgNO_3$) (*Argenti Nitras, Lunar Caustic*).—Concentrated nitric acid dissolves pure silver, and on evaporation leaves colorless crystalline plates. These are readily soluble, have a metallic taste, and are stable apart from organic matter, but with it they blacken by reduction to metallic silver. It forms insoluble compounds with albumin, and hence is a superficial caustic, producing a shallow eschar, which soon blackens. This quality makes it useful as a hair dye and an indelible ink. To obviate brittleness the crystals are melted with 4 per cent. hydrochloric acid and cast in sticks called *argenti nitras fusus.* For mild local use stick caustic is sometimes diluted with potassium nitrate, making *mitigated nitrate, argenti nitras mitigatus*, U. S. P. The *incompatibles* are alkalis, alcohol, chlorids, acetates, bromids, iodids, carbonates, cyanids, arsenites, salts of antimony, copper and manganese, vegetable extracts, phosphates, sulphids, tannic acid, and vegetable astringents.

Silver cyanid, U. S. P., ($AgCN$), is precipitated as a white solid when argention meets cyanidion $(CN)^-$:

$$Ag^+, (NO_3) \quad + \quad K^+, (CN)^- \quad = \quad K^+, (NO_3)^- \quad + \quad AgCN.$$

By adding excess of potassium cyanid a soluble double salt is formed:

$$AgCN \quad + \quad K^+, (CN)^-, \quad = \quad K^+, [Ag(CN)_2]^-.$$

This solution fails to give the ordinary silver reactions because it has no argention, the metal being locked up in the silver cyanidion $[Ag(CN)_2]^-$. In electroplating with this solution the double salt breaks down and the silver goes to the object at the negative pole to be deposited as a uniform metallic coating.

Toxicology.—Of 7 cases reported due to accidental swallowing of the caustic when applied to the throat for local affections, 5 were in children (1 of these was fatal) and 2 in adults.

Symptoms.—The contact of the caustic causes instant pain in the throat and stomach, prompt emesis, and later purging of bloody matters. After absorption takes place, nervous symptoms supervene, such as vertigo, spasms, disturbed respiration, and coma.

Chronic Poisoning.—Repeated cauterization with silver nitrate caused the following effects: Emaciation, followed in a few weeks by paralysis and other nervous affections, with ecchymoses under the eyelids. The face turned a leaden color, the sclerotics were discolored, many brown-black spots appeared all over the body, and a blue line was seen on the gums. Similar discoloration patches, oval and about the size of apple seeds, have been found in silver workers, and are attributable to absorption through abrasion of the hands. The patches proved to be due to deposit of metallic silver in the tissues.

A leaden-bluish discoloration of the face and possibly of other parts of the body is sometimes brought on by the medicinal use of small doses of silver nitrate given for a long period. No manner of treatment is of any avail to remove this discoloration.

Fatal Dose.—Death has resulted from 30 gr. taken by an adult.

Fatal Period.—In six hours after swallowing a piece of "lunar caustic" a child of fifteen months died in convulsions.

Treatment.—Large drafts of common salt and water will favor vomiting and at the same time be the best antidote, forming insoluble silver chlorid. The stomach-pump may be used, if necessary. This treatment can be followed up with a diet of eggs and milk.

Postmortem Appearances.—The local action of the caustic will be seen in stains, at first white, and on exposure to light,

turning black. These stains are found on the lips, in the mouth, on white clothing, and on the mucous membrane of the digestive tract touched by the poison. Gastro-intestinal inflammation is present.

Tests.—**Hydrochloric acid** and **soluble chlorids** precipitate from soluble salts of silver, white-silver chlorid, insoluble in nitric acid, but readily soluble in ammonia-water and in potassium cyanid.

Hydrogen sulphid or **ammonium sulphid** precipitates a dark brown silver sulphid in accordance with this equation:

$$2AgNO_3 + H_2S = Ag_2S + 2HNO_3.$$

Potassium iodid gives a yellow precipitate, and **potassium chromate** a blood-red precipitate.

Extraction from Stomach Contents.—Finely divided tissues or gastric contents are digested with ammonia and potassium cyanid. The decanted fluid is treated with excess of hydrochloric acid and the insoluble chlorid separated by decantation; the precipitate is washed on a filter with hot water, dried, and reduced on charcoal to metallic silver.

VI.—THE IRON GROUP

This group includes iron, cobalt, nickel, manganese, zinc, and chromium, heavy metals whose sulphids are insoluble in water, but are soluble in dilute acids.

IRON (Ferrum)

Symbol, Fe. Atomic weight, 55.85.

Iron is the most important of the metals, because of the abundance of its ores, the ease of its extraction, and the value of its properties.

Occurrence.—Iron ranks next to aluminium in abundance in the crust of the earth. Rarely it occurs free in nature in two forms, *meteoric* and *telluric*. The metal of fallen meteorites is never pure, as it contains cobalt, nickel, and other metals. The telluric kind is found in small quantities in lavas and basalt. Its most common ores are oxids, such as *magnetic oxid*, Fe_3O_4; *red hematite*, Fe_2O_3; *carbonate*, $FeCO_3$; and sulphids or *iron pyrites*, FeS_2; *magnetic pyrites*, FeS_4; *copper pyrites*, $CuFeS_2$.

Nearly all rocks contain *silicate of iron*, which, decomposing to

oxid, imparts a red color to the soil. Plants absorb the iron and store it in the green chlorophyl of leaves, which is essential to the interaction of carbon oxid, water, and oxygen, by which the tissues are built up. Having served the respiratory function of the plant, iron is assimilated by animals from their vegetable food, stored in the liver as a loose compound called *ferratin*, from which it is taken as required to become a necessary constituent of the hemoglobin which carries the oxygen of respiration to the animal tissues. It is eliminated from the body as a constituent of bile coloring-matter. In animals and plants its physiologic importance appears to be due to a catalytic influence exerted, by which it accelerates the oxidation processes.

In extracting the metal from its carbonate, sulphid, and hydroxid the ore is roasted in air, evolving from sulphids, SO_2; carbonates, CO_2; hydroxids, steam; all of these escaping as gases. From the oxid simple reduction with carbon suffices:

$$Fe_3O_4 + 4C = 4CO + 3Fe.$$

Limestone or sand and feldspar are also heated with the ores in order to take up impurities and protect the metal when it is freed. As molten metal it is received in molds in sand. This crude *pig iron* always contains some carbon, silicon, sulphur, phosphorus, and other impurities. *Cast iron* contains about 5 per cent. of carbon. It melts at a lower temperature than pure iron, is not so hard as steel, and is more brittle than wrought iron. By melting again and blowing in air some of the carbon, phosphorus, sulphur, etc., is burned out and a purer product obtained called *wrought iron*. This is tough, strong, malleable, and ductile, and contains less than 0.5 per cent. of carbon. It welds easily, but is soft and bends under strain. When cast iron is melted and purified by oxidation and then, by the addition of iron containing carbon, converted into a product containing between 0.8 and 2 per cent. carbon, we have *steel*. When steel is heated and suddenly cooled it becomes extremely hard and brittle. If carefully heated and then cooled slowly, it becomes soft and elastic. In its soft state steel can be given the shape desired and by *tempering* at different temperatures the hardness can be regulated to the degree required for the uses of the instrument.

Properties.—Pure iron is silver white and susceptible of a high polish. It is more malleable, softer, and less tenacious than wrought iron. Its specific gravity is 7.84. It melts only at the highest temperatures, but at a lower point—about 600° C. (1112° F.)—it becomes plastic like wax, and can be pressed, rolled, forged, and welded. In dry air it is unchanged at ordinary temperatures,

but at a red heat it oxidizes. In moist air it forms a *rust* of hydrate and oxid. *Galvanized iron* is made so by dipping the iron into molten zinc to protect it from moisture. The purest commercial form is card teeth or piano wire.

Reduced iron (*Ferrum reductum, Quevenne's iron, iron by hydrogen*) is prepared by heating the oxid, Fe_3O_4, in a current of hydrogen. The hydrogen abstracts oxygen to form water, leaving a gray-black powder, odorless, tasteless, and insoluble. Dose: 1 to 5 gr. (0.066–0.333 gm.). *Incompatible* with potassium chlorate and permanganate; hydrogen dioxid; salts of antimony, copper, bismuth, lead, mercury, and silver.

Iron dissolves in hydrochloric acid, forming a chlorid, and in dilute sulphuric acid, forming a sulphate, in each case liberating hydrogen. The electric charge of the hydrion has changed the iron to ferrion. It unites directly with the halogens, sulphur, phosphorus, arsenic, and antimony. When dipped into concentrated nitric acid it becomes *passive.* Some electric condition is induced which protects it from further action by either dilute or strong nitric acid.

Ferrous and Ferric Ions.—There are two kinds of elementary ions formed by iron, one divalent, *diferrion*, the other trivalent, *triferrion.* The compounds of the former are similar to those of magnesium and are called *ferrous;* those of the latter resemble aluminium salts and are called *ferric.* Diferrion has an inky taste and is colorless, but in aqueous solution forms greenish ferrous hydroxid. It has a tendency to pass into triferrion, also colorless, but in water forming brown ferric hydroxid. This brown hydroxid is in colloidal solution, having been split off from the ferric salt by hydrolytic dissociation. When diferrion, Fe^{++}, changes to triferrion, Fe^{+++}, by the action of oxidizing agents it receives an additional ionic charge which, under favorable conditions, it surrenders to reducing agents, passing back to the divalent form, Fe^{++}. The effect of exposure of a ferrous solution to the air is to cause oxygen and water to form hydroxidion, the negative ion needed to give to diferrion its increased positive charge. The change takes place in the sense of the following equations:

$$\underset{\text{Ferrous chlorid.}}{3FeCl_2} + O + H_2O = \underset{\text{Ferric chlorid.}}{2FeCl_3} + \underset{\text{Ferrous hydroxid.}}{Fe(OH)_2}$$

The ferrous hydroxid with the co-operation of water takes more oxygen and forms the ferric hydroxid:

$$\underset{\text{Ferrous hydroxid.}}{2Fe(OH)_2} + O + H_2O = \underset{\text{Ferric hydroxid.}}{2Fe(OH)_3}$$

Ferrous Chlorid ($FeCl_2$) (*Iron Protochlorid*).—When iron is heated in a current of dry hydrochloric-acid gas a white salt is obtained. This anhydrous compound takes up 4 parts of water of crystallization, turning green in color. When excess of iron is dissolved in hydrochloric acid a pale green solution of the ferrous chlorid is formed. The dissociation of ferrous chlorid in solution is represented thus: Fe^{++}, Cl^-, Cl^-. When chlorin is passed into the solution the cation Fe^{++} takes a third ionic charge, the chlorin neutral atom changing to the anion chloridion:

$$Fe^{++}Cl^-, Cl^- + Cl = Fe^{+++}Cl^-, Cl^-, Cl^-.$$

This is an illustration of the fourth mode of ion formation; where an atom changes to an ion, at the same time giving an additional charge of electricity to an ion already present. It is called *oxidation* in the sense that it increases the electric charges of an ion; whereas *reduction* diminishes the charges. When the above equation is reversed it represents reduction.

Ferric Chlorid ($FeCl_3,6H_2O$) (*Ferri Chloridum, Sesquichlorid,* or *Perchlorid*).—The pharmaceutic product is prepared by adding to a solution of ferrous chlorid nitric and hydrochloric acids with heat. Fumes of nitrogen dioxid are formed:

$$FeCl_2 + HNO_3 + HCl = FeCl_3 + H_2O + NO_2.$$

On evaporation the ferric chlorid is obtained as an orange-yellow deliquescent mass of acid reaction and strongly styptic taste.

The pure anhydrous ferric chlorid is obtained as a sublimate of dark green crystals when iron is heated in a current of chlorin. They dissolve in water with a rise of temperature yielding a yellow-brown solution from which the anhydrous salt cannot be again obtained. By evaporation yellow hydrates crystallize which by heat decompose to HCl and $Fe(OH)_3$.

In the presence of substances which oxidize readily, such as morphin, ferric chlorid decomposes water, sets free available oxygen, and is itself reduced to ferrous chlorid thus:

$$2FeCl_3 + H_2O = 2FeCl_2 + 2HCl + O.$$

Liquor ferri chloridi is an aqueous solution of ferric chlorid containing 37.8 per cent. of anhydrous salt with some free hydrochloric acid. It is a reddish-brown, acid, astringent liquid of a specific gravity of 1.405.

Tinctura ferri chloridi (*muriated tincture of iron*) is prepared by mixing the above solution with 3 volumes of alcohol and keeping

in a stoppered bottle for three months. From the alcohol certain ethereal compounds are produced which impart to the acid brownish liquid their odor, taste, and medicinal effect. It contains 13.28 per cent. of $FeCl_3$. This is a valuable ferruginous tonic, which should be taken freely diluted in water, syrup, or glycerin, and through a tube to prevent action on the teeth. Dose: 5 to 20 ♏ (0.33–1.33 c.c.). Its *incompatibles* are mucilage of acacia, astringent infusions and tinctures, tannic acid, antipyrin, and alkalis and their carbonates.

Ferric Hydroxid (*Ferric Hydrate, Ferri Oxidum Hydratum*).—When alkaline bases are added to solutions of ferric salts, a brown, flocculent, gelatinous precipitate of ferric hydroxid is obtained:

$$FeCl_3 \quad + \quad 3NaHO \quad = \quad Fe(OH)_3 \quad + \quad 3NaCl.$$

The fresh hydroxid is soluble in acids and in solution of ferric chlorid. On standing it assumes less soluble forms, growing denser and to some extent giving up the constituents of water, thus:

$$2Fe(OH)_3 \quad = \quad Fe_2O_3 \quad + \quad 3H_2O.$$

When freshly precipitated and strained off in a state of loose magma it is an efficient antidote to arsenic, but the anhydrid change that occurs in time lessens materially its virtue in this respect:

$$Fe(OH)_3 \quad + \quad \underset{\text{Arsenous acid.}}{H_3AsO_3} \quad = \quad \underset{\text{Ferric arsenite.}}{FeAsO_3} \quad + \quad 3H_2O.$$

Ferri Hydroxidum cum Magnesii Oxido (U. S. P.).—This is made by mixing, when required, an excess of calcined magnesia with solution of ferric sulphate:

$$Fe_2(SO_4)_3 + 3MgO + 3H_2O = 2Fe(OH)_3 + 3MgSO_4.$$

The whole mixture of ferric hydroxid, magnesium sulphate, and some excess of magnesium oxid is of service and may be given immediately without straining.

Dialyzed Iron (*Ferrum Oxydatum Dialysatum*).—This is a 5-per cent. solution of colloidal ferric hydroxid once used in medicine. It is prepared by adding ammonium hydroxid to a concentrated solution of ferric chlorid. The ferric hydroxid first formed dissolves in the ferric chlorid when shaken. This saturated solution of basic oxychlorid of iron is put in a dialyzer having a partition of parchment-paper, and floated on water. The ammonium chlorid quickly diffuses into the water, which is frequently renewed, until there is no reaction with silver nitrate. There is hydrolytic dissociation of part of the ferric oxychlorid into hydro-

chloric acid which, when split off, passes out through the membrane, and colloidal ferric hydroxid which remains in the dialyzer with some trace of chlorid. In the dialyzer is left a dark red colloidal solution (the *dialysate*), the constituents of which are not dissociated, having in that state none of the properties of the ferric ion. It instantly separates the insoluble gelatinous hydroxid on the addition of an electrolyte, such as alkalis, neutral salts, and sulphuric acid (p. 93).

Ferrous Iodid (FeI_2).—Elementary iodin in excess and metallic iron as card teeth unite directly in the presence of warm water, forming a pale green solution. On evaporation greenish crystals of ferrous iodid separate. In air the iodid readily decomposes, forming ferric oxid, but if protected by sugar the oxidation is prevented. In the following preparations sugar is introduced for the purpose of keeping the ferrous salt from changing to ferric compounds which have more astringency and irritating quality:

Pilulæ ferri iodidi (*Blancard's pills*) not only have sugar in the pill-mass, but are further protected by a coating of balsam of tolu.

Syrupus ferri iodidi is a syrupy solution of 5-per cent. ferrous iodid, transparent, greenish, and neutral. Dose: 5 to 50 ♏ (0.33–2 c.c.).

Ferrous Sulphid (FeS).—When iron filings and flowers of sulphur are heated together a black brittle mass is formed of the composition, FeS. Its chief use is in the preparation of hydrogen sulphid. As it is readily decomposed by acids, it is not precipitated when hydrogen sulphid is passed into ferrous solutions. The proper precipitant for the iron group is ammonium sulphid, which yields black hydrated iron sulphid. Ferrous sulphid in the air oxidizes to ferrous sulphate:

$$FeS \quad + \quad 4O \quad = \quad FeSO_4.$$

Ferrous Sulphate ($FeSO_4 . 7H_2O$) (*Ferri Sulphas, Copperas, Green Vitriol*).—The term *vitriol* is applied to metallic sulphates of divalent ions; thus, copper sulphate is *blue vitriol* and zinc sulphate is *white vitriol.* Ferrous sulphate can be obtained by the action of dilute sulphuric acid on iron. The solution evaporated yields large pale green prismatic crystals, having a styptic taste and acid reaction. In the air it effloresces, absorbs oxygen, and partially changes to brown ferric sulphate. It is *incompatible* with vegetable astringents, tannic acid, alkalis, borax, lime-water, carbonates, ammonium and calcium chlorid, lead acetate, potassium iodid, and nitrate.

Ferri Sulphas Exsiccatus ($FeSO_4 . H_2O$).—Dried sulphate is prepared by heating ferrous sulphate at 100° C. (212° F.) until

it ceases to lose weight. It is a grayish white powder, useful in making pills. Dose: $\frac{1}{2}$ to 2 gr. (0.033–0.133 gm.).

Ferri sulphas præcipitatus, granulated, is ferrous sulphate separated as a crystalline powder from solution in weak sulphuric acid by mixing with alcohol. It is a convenient form for dispensing.

Liquor ferri tersulphatis is a 36-per cent. solution of *normal ferric sulphate*, $Fe_2(SO_4)_3$, and is made by heating a solution of ferrous sulphate with sulphuric and nitric acids. The nitric acid oxidizes diferrion to triferrion. On evaporating and heating the residue a yellowish white powder is obtained. Placed in water, it at first does not dissolve, but after some time it forms a strong brown-red solution. Because of this slow solubility the salt is usually kept in the official solution ready made.

Monsel's salt is a basic, or oxy-, sulphate used in surgery as a local hemostatic. It is a yellowish powder obtained by evaporation from Monsel's solution, which is the official *liquor ferri subsulphatis*, containing 43.7 per cent. of the salts. This solution is prepared like that of the normal sulphate, but with less sulphuric acid. It is supposed to contain ferric hydroxid, $Fe(HO)_3$, joined to ferric sulphate, $Fe_2(SO_4)_3$. It is a dark, reddish brown, highly astringent, almost syrupy solution, causing but little local irritation.

Ferric Nitrate ($Fe(NO_3)_3$).—By dissolving ferric hydroxid in nitric acid a solution of this salt results, which when 6 per cent. strong is called *liquor ferri nitratis*. It is transparent, amber colored, acid, and styptic. Dose: 5 to 15 ♏, well diluted (0.33–1 gm.).

Ferrous carbonate, $FeCO_3$, occurs in nature as "bog ore." Insoluble in pure water, it dissolves in natural carbonated waters by changing to a soluble ferrous bicarbonate, $FeH_2(CO_3)_2$. It is formed when alkaline carbonates act on ferrous salts:

$$FeSO_4 + Na_2CO_3 = Na_2SO_4 + FeCO_3.$$

The precipitate is whitish green, turning brown-red by oxidation. To prevent this change to the ferric condition sugar is used in the following official preparations which make use of the same reaction as that given above:

Ferri carbonas saccharatus contains 15 per cent. of $FeCO_3$. It is a greenish gray powder, sweet and ferruginous in taste. Dose: 2 to 10 gr. (0.13–0.66 gm.).

Massa ferri carbonatis (*Vallet's mass*) contains 42 per cent. $FeCO_3$. It is unirritating and not astringent. Dose: 3 to 5 gr. (0.20–0.33 gm.).

Mistura ferri composita (*Griffith's mixture*) contains ferrous carbonate suspended in a solution of potassium sulphate with sugar and rose-water. Dose: ½ to 1 fl. oz. (16–32 c.c.).

Ferrous Phosphate ($Fe_3(PO_4)_2$).—This is formed when sodium phosphate is added to ferrous sulphate in the presence of sodium acetate. At first white, it absorbs oxygen and soon assumes a blue color. It is the source of the slaty-blue color of pus and of the lungs in phthisis.

Ferric phosphate, $FePO_4$, is precipitated when ferric chlorid is added to a solution of an alkali phosphate. It is official in the *ferri phosphas solubilis*, a soluble mixture of $FePO_4$ with sodium citrate. Dose: 5 to 10 gr. (0.33–0.66 gm.).

Ferri pyrophosphas (U. S. P.) is a soluble mixture in the form of scales containing ferric pyrophosphate, sodium citrate, and ferric citrate. Dose: 1 to 5 gr. (0.066–0.33 gm.).

Scale Compounds.—When freshly precipitated ferric hydroxid is dissolved in citric, tartaric, or other organic acid, double salts are formed of uncertain composition. On evaporating the solution the residue is not crystalline. To obtain a convenient form for dispensing the solution concentrated by evaporation is spread on glass plates and dried at 60° C. (140° F.). By tapping the glass the thin coating is broken into green or brown amorphous brilliant scales, which readily dissolve in water. Among the scale compounds are *soluble iron phosphate*, *iron* and *quinin citrate*, *iron* and *potassium tartrate*.

Iron and Cyanogen.—These two elements do not unite to form a ferric cyanid, but combine in complex groups which act as anions with hydrogen and the metals. As these groups do not show the chemical or poisonous properties of cyanids nor respond to the usual tests for iron, it is plain that they do not contain the ions of cyanogen or of iron. One of these compound anions acting like a single element is called *ferrocyanogen*, and its solution becomes ferrocyanidion, $Fe(CN)_6^{\equiv}$. It does not exist free, but is supposed to be the constituent anion of *hydroferrocyanic acid*, H^+, $[Fe(CN)_6]^{\equiv}$, and enters into the composition of metallic ferrocyanids. This tetrabasic acid is prepared by the action of strong hydrochloric acid on potassium ferrocyanid. It occurs in white scales, turning blue on exposure to the air.

Potassium Ferrocyanid ($K_4Fe(CN)_6$) (*Yellow Prussiate of Potash*).—This is prepared by heating together nitrogenous animal waste, scrap iron, and potassium carbonate. The permanent lemon-yellow crystals are freely soluble and non-poisonous, though they form hydrocyanic acid when heated with sulphuric acid. Potassium ferrocyanid is used to precipitate ferrocyanids from

many metallic salts, giving in acid solutions of cobalt a *yellowish green* precipitate; of uranium, a *brown;* of copper, a *chocolate;* of barium, a *yellowish white;* and a *white* precipitate from zinc, nickel, tin, cadmium, lead, antimony, bismuth, silver, mercury, and manganese. With ferrous salts it yields *white* precipitates; passing from *light blue* to *dark blue;* with ferric salts *dark blue* ferric ferrocyanid.

The ion Fe^{++} is precipitated from ferrous solutions by hydrogen sulphid, but is not precipitated by this reagent from the solutions of potassium ferrocyanid, since on dissolving this salt the complex ferrocyanidion $[Fe(CN)_6]^{\equiv}$ is formed and not diferrion Fe^{++}.

Ferric ferrocyanid, $Fe_4[Fe(CN)_6]_3$, is a highly valued pigment known commercially as *Prussian blue.* It is formed whenever triferrion, Fe^{+++}, meets ferrocyanidion; and as the dark blue color is recognizable in very small quantities, it makes a very sensitive reaction for ferric salts.

Ferricyanogen is a hypothetic group not existing free, but present as anion in hydroferricyanic acid, H^+_3, $[Fe(CN)_6]^{\equiv}$, and metallic ferricyanids. The anion has the same composition as in ferrocyanids, but differs in being trivalent, while ferrocyanidion is tetravalent. Like the latter, ferricyanidion exhibits none of the chemical or physiologic properties of either cyanogen or iron.

Hydroferricyanic acid, $H_3Fe(CN)_6$, can be obtained from solutions of its salts, in brown needles, by the action of strong hydrochloric acid. It is tribasic.

Potassium ferricyanid, $K_3Fe(CN)_6$ (*red prussiate of potash*), is prepared from the ferrocyanid by treating it with oxidizing agents, such as chlorin:

$$K_4Fe(CN)_6 \quad + \quad Cl \quad = \quad K_3Fe(CN)_6 \quad + \quad KCl.$$

Garnet red crystals separate as the solution is concentrated. The dry crystals are permanent, but the solution is unstable and must be made fresh when used as a reagent. With neutral solutions of metallic salts it yields precipitates which differ in color from those given by potassium ferrocyanid. The most important of these, showing that the solution contains diferrion, is *ferrous ferricyanid,* $Fe_3[Fe(CN)_6]_2$, a bright blue precipitate called *Turnbull's blue.*

Ferric sulphocyanate ($Fe(SCN)_3$) (*thiocyanate*) is the cause of the deep blood red color formed when an excess of potassium thiocyanate, KSCN, is added to solution of a ferric salt. The most pronounced reaction is obtained by having a great concentration of thiocyanate, which drives back the relatively small amount of triferrion into the red undissociated state. The effect

is enhanced by shaking with ether, which dissolves and separates the red undissociated ferric thiocyanate.

Sodium nitroprussid, $Na_2Fe(CN)_5NO \cdot 2H_2O$, occurs in ruby-red crystals formed when sodium ferrocyanid is treated with nitric acid. It is used in Legal's test for acetone in the urine. With alkaline sulphids it turns purple.

Liquor ferri acetatis is a 33-per cent. aqueous solution of normal ferric acetate, $Fe(C_2H_3O_2)_3$. It is a deep red, transparent liquid of acetous odor and sweet ferruginous taste. It is used to prepare *tinctura ferri acetatis*, which has, in addition to the above, alcohol and acetic ether.

Liquor ferri et ammonii acetatis, or *Basham's mixture*, is an agreeable preparation containing tincture of ferric chlorid, ammonium acetate, and acetic acid dissolved in a sweetened elixir of orange. Dose: 2 to 4 fl. dr. (8–16 c.c.).

Toxicology of Iron Salts.—Although iron is present in the body, also in food, and is a frequent constituent in tonic medicines, yet sufficient evidence exists that at least two of its salts, ferrous sulphate and ferric chlorid, have toxic properties when taken in excessive doses. Diarrhea and abdominal pain mark the course of a gastro-enteritis.

The widely used preparation *tinctura ferri chloridi*, or "tincture of iron," a brown acid liquid, is frequently mistaken for harmless liquids of the same color. It has been taken in toxic doses as an abortifacient.

Symptoms.—When ferric chlorid has been given experimentally to the lower animals with food it has been found harmless even in considerable doses. The same amounts given fasting and in alcoholic solution have resulted in death in from one to sixteen hours. It causes an inky, metallic taste, violent abdominal pain, vomiting, diarrhea, paralysis of the extremities, suppression of urine, convulsions, and death. The feces are blackened by the iron sulphid formed.

Fatal Dose.—One case has been reported of death after five weeks from a dose of the chlorid equal to $1\frac{1}{2}$ oz. of the "tincture of iron." An ounce has caused vomiting and urinary symptoms. On the other hand, a man aged seventy-two recovered from the effects of 3 oz. of the tincture.

Treatment.—The alkaline bicarbonates or the carbonates dissolved in a large amount of water or milk may be swallowed or used to wash out the stomach with a pump or tube. The gastro-enteric symptoms should be treated by rest and anodynes.

Postmortem Appearances.—In one case a greenish black, fur-like "mud" covered the tongue, esophagus, and stomach; swelling, congestion, and ecchymotic points were the changes noted

in the liver and kidneys, and hyperemia marked the brain and its membranes.

Tests.—Ammonium sulphid causes a black precipitate of iron sulphid with solutions of ferrous or ferric salts. It can be used after the metal has been extracted from the tissue with acetic acid. The equation for this reaction is:

$$FeSO_4 + (NH_4)_2S = (NH_4)_2SO_4 + FeS.$$

Redissolving the sulphid in nitrohydrochloric acid, the iron will yield to *potassium ferrocyanid* a blue precipitate. If the iron solution is almost neutralized with ammonia, then *ammonium sulphocyanid* will give a red color.

The analytic reactions which distinguish diferrion from triferrion may be summarized according to the following scheme, using ferrous sulphate for the former and ferric chlorid for the latter. In aqueous solution the ferrous salt is light green and ferric salt reddish brown. With the reagent named in the first column the precipitates yielded are stated in the other columns:

Reagents.	Ferrous salts.	Ferric salts.
Hydrogen sulphid.	No precipitate.	White precipitate of sulphur, and reduction to ferrous state.
Ammonium sulphid.	Black precipitate.	Black precipitate.
Alkalis.	White precipitate, turning green.	Red-brown precipitate.
Potassium ferrocyanid.	White precipitate, turning blue.	Prussian-blue precipitate.
Potassium ferricyanid.	Dark blue precipitate.	Green color, but no precipitate.
Potassium sulphocyanid.	No precipitate.	Blood-red color.
Acid tannic.	No change.	Greenish-black, inky precipitate of ferric tannate.

Detection.—Having digested the organic matters thoroughly in water acidulated with acetic acid, filtered, evaporated the filtrate to dryness, and incinerated the residue, the ash is treated with dilute sulphuric acid and the solution tested as above with ammonium sulphid and potassium ferrocyanid. Determination of poisonous amounts must rest upon the quantity found in the organs in excess of that normally present. The black fur on the mucous membranes and the stains on the clothing ought to yield significant amounts.

MANGANESE

Symbol, Mn. Atomic weight, 54.93.

Manganese occurs in nature usually as an oxid, the most abundant being *pyrolusite*, MnO_2. The metal can be made by electrolysis of the chlorid or by reduction of the oxid by heating with carbon or with powdered aluminium.

The metal belongs to the iron group, because of its similarity in physical and chemical properties. When pure it is reddish gray in color, lustrous, and resists the action of the air fairly well, but the impure form rusts more easily than iron and has little commercial value except as an alloy of iron and bronze.

Manganese Dioxid (MnO_2) (*Black Oxid of Manganese*).—Of the seven oxygen compounds this is the only one of much importance. It is a heavy, black crystalline mineral; its chief use in the arts being that of an oxidizing agent, as in the manufacture of chlorin from hydrochloric acid (see Chlorin, p. 118). Compressed into a cylinder with carbon it is used as the negative element of a *Leclanché battery cell* (p. 47). The energy of this cell is derived largely by the loss of charges of electricity when Mn^{++++} changes to ions of lower valence.

Ions of Manganese.—In the case of the dioxid, manganese is tetravalent. The series of salts of the lowest valence are called *manganous*, in which occurs the divalent ion, Mn^{++}. These differ from the ferrous salts in that their acid solutions do not absorb oxygen from the air. *Dimanganion* is distinctly basic and has a pale reddish color. Trivalent manganese, Mn^{+++}, is weakly basic and occurs in the *manganic* compounds into which the manganous pass by oxidation. The color of its unstable solutions is violet-red. Its salts quickly hydrolyze into brown manganic hydroxid, $Mn(OH)_3$.

Manganous Sulphid (MnS).—The pink precipitate formed when ammonium sulphid is added to a cold solution of a manganous salt is a hydrate of manganous sulphid. On standing it becomes dehydrated and changes to green manganous sulphid. This green sulphid is precipitated immediately when the manganous solution is hot and concentrated.

Manganous Sulphate ($MnSO_4 \cdot 4H_2O$) (*Mangani Sulphas*).—This is produced when oxygen is generated by the "wet way," dissolving manganese dioxid in sulphuric acid:

$$MnO_2 \quad + \quad H_2SO_4 \quad = \quad MnSO_4 \quad + \quad H_2O \quad + \quad O.$$

When purified from iron it forms pale rose-colored prisms with an astringent bitter taste. The crystals are soluble in water. Manganous sulphate is used as a tonic adjuvant to iron. Dose: 2 to 5 gr. (0.13–0.33 gm.).

Hexavalent manganese is known in the salts of *manganic acid*, H_2MnO_4, which is regarded as formed from $Mn(OH)_6$ by loss of $2H_2O$. The acid itself is so unstable that it does not exist free, but its salts, such as potassium manganate, K_2MnO_4, are stable in alkaline solutions. In acid or neutral solutions they instantly change to salts of permanganic acid. The solution of

crude potassium manganate with some potash has a green color, but on exposure to the air absorbs carbon dioxid, changes to potassium permanganate, $KMnO_4$, and passes from green to purplish red through violet and blue. This play of colors gave the substance the name *mineral chameleon*:

$$\underset{\text{Potassium manganate.}}{3K_2MnO_4} + 2CO_2 = MnO_2 + 2K_2CO_3 + \underset{\text{Potassium permanganate.}}{2KMnO_4}$$

Potassium Permanganate ($KMnO_4$).—This is the purple-red crystalline product obtained on evaporation of the red liquid just mentioned above. The anion here is the univalent permanganic ion $(MnO_4)^-$, analogous to the perchloric $(ClO_4)^-$. In the manganates the anion $(MnO_4)^=$ is divalent. Permanganic acid is the highest stage of oxidation and may be regarded as the partial anhydrid of *heptavalent* manganese in the hydroxid $Mn(OH)_7$:

$$Mn(OH)_7 \text{ less } 3H_2O = HMnO_4.$$

This salt is a powerful oxidizing agent for almost all organic substances, and is destructive to the low organisms of infectious diseases. Its solutions should not be kept in contact with rubber or cork nor filtered through paper, or the brown manganese hydroxid will form. The brown stains made by it can be removed by oxalic or hydrochloric acid.

"Condy's disinfecting fluid" is a 2-per cent. solution of it and "Darby's fluid" also contains it.

With alkalis in the presence of reducing agents 2 molecules of potassium permanganate yield 3 atoms of oxygen. The decomposition is according to this equation, in which X is the organic substance:

$$2KMnO_4 + 5H_2O + X = 2KOH + 2Mn(OH)_4 + XO_3.$$

With acids the salt yields to reducing agents 5 oxygen atoms:

$$2KMnO_4 + 3H_2SO_4 + X = K_2SO_4 + 2MnSO_4 + 3H_2O + XO_5.$$

It oxidizes oxalic acid to carbon dioxid and water in such exact proportions that its solution is used for volumetric testing of that substance, and conversely the oxalic acid is used to standardize solutions of permanganate which tend to deteriorate for a short length of time.

$$C_2H_2O_4 + O = 2CO_2 + H_2O.$$

One molecule of oxalic acid requires one atom of oxygen; therefore, one liter of normal solution of oxalic acid is exactly oxidized by a liter of normal permanganate solution. The oxalic acid

decolorizes the permanganate until the acid is all oxidized; if the purple color persists, it shows plainly the end of the reaction.

The oxidizing powers of this salt are brought into action when it is used as an *antidote* to the poisonous alkaloids, with which it reacts more promptly than with the usual gastric contents. As an antidote 1 or 2 gr. are given dissolved in 1 pt. of water, and then removed by the stomach-tube or emetics. When administered in pills the excipient should be unoxidizable substance, such as kaolin and petrolatum. It decomposes alcohol and oxidizes glycerin and turpentine with a rapidity that is almost explosive. The other *incompatibles* are organic substances, alkaloids, acids, charcoal, carbolic acid, chlorids, bromids, arsenites, mercurous and ferrous salts, ammonia, hydrogen dioxid, sulphites and hyposulphites, also phosphites and hypophosphites.

Tests for Manganese Salts.—With *ammonium sulphid*, manganous sulphate yields a *flesh-colored* precipitate soluble in acids.

With *ammonium* or *sodium hydroxid* there results a *white* manganous hydroxid which oxidizes in the air to a brownish color and dissolves pink in oxalic acid.

A small portion of gray manganese compound placed on platinum foil and heated with a mixture of sodium nitrate and carbonate, fuses to make sodium manganate, which yields a green aqueous solution, changing to red on the addition of an acid.

CHROMIUM

Symbol, Cr. Atomic weight, 52.

This is a white, hard, crystalline metal of difficult fusibility. Though readily attacked by alkalis, it resists all acids except hydrochloric. It forms salts of divalent dichromion, Cr^{++}, called *chromous*, and of trivalent trichromion, Cr^{+++}, called *chromic*.

The ion of chromous compounds is blue and strongly reducing in its effect, passing into the ion of chromic salts.

Chromium hydroxid, $Cr(OH)_3$, is a green precipitate formed when ammonia acts on solutions of green chromic salts. It dissolves in excess of the alkali to a green liquid. One of the hydroxids is known as *chromium green*, $Cr_2O(OH)_4$, an emerald pigment used in the arts; it is non-poisonous.

Chromic oxid (Cr_2O_3) (*sesqui-oxid*) is green, insoluble, and is not easily fused or decomposed by heat. With alkaline hydroxids and nitrates it forms chromates in two series: one green, the other violet. The hydroxid formed by alkalis from the violet salt is violet in color.

Chromanion.—Heated in the air with strong bases, chromium compounds take up oxygen and form chromates. These are salts

of a bivalent anion $(CrO_4)^=$, which is isomorphous with sulphanion, $(SO_4)^=$. This chromanion imparts its yellow color to its salts; such as the potassium chromates and lead chromate.

Chromic anhydrid, CrO_3, with water forms true chromic acid, H_2CrO_4. In this acid the chromium, like the manganese in manganic acid, has the valence of six, and in $HCrO_5$, *perchromic acid*, a yet higher valence. A solution of potassium dichromate and sulphuric acid treated with a few drops of hydrogen dioxid is oxidized and yields the transient blue color of perchromic acid, which changes quickly as it evolves oxygen. But, shaken with ether, the blue color persists longer in the separate ethereal extract (p. 89).

Potassium chromate (K_2CrO_4) (*neutral chromate*) is sulphur yellow, crystalline, and soluble. Its aqueous solution is alkaline. When any acid containing hydrion is added, the color changes from yellow to orange, and the salt that crystallizes out is the dichromate, $K_2Cr_2O_7$.

$$2K_2CrO_4 + H_2SO_4 = H_2O + K_2SO_4 + K_2Cr_2O_7.$$

Chromanion $(CrO_4)^=$ is changed to dichromanion $(Cr_2O_7)^=$ as indicated in this equation:

$$2(CrO_4)^= + H^+ + H^+ = H_2O + (Cr_2O_7)^=.$$

Potassium dichromate, $K_2Cr_2O_7$, occurs in orange-red soluble crystals used by dyers and furniture stainers. Operatives in chemical works find that in the shape of fine aërial particles it irritates the respiratory passages, sets up ozena, and causes eruptions and excoriations leading to chronic ulcers.

Chromium trioxid (CrO_3) (*chromic acid, chromic anhydrid*) is prepared by the action of sulphuric acid on saturated solution of potassium dichromate:

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + 2CrO_3 + H_2O.$$

It occurs in crimson prismatic needles, deliquescent, freely soluble, and in strong solution is acid and acts on organic matter with energy. This violent reaction with organic matter is the basis of the usual *caution* against using cork stoppers or mixing it with alcohol, ether, or glycerin. It is also *incompatible* with arsenous acid, chlorids, bromids, iodids, sulphids, oxalates, sulphites, and tartrates. Its only use in medicine is external, as a deep caustic to the tonsils, and to papillary growths. When applied to fungous growths in the mouth a portion is sometimes

accidentally swallowed. It causes an acrid taste and burning in the throat, with persistent vertigo, vomiting of a ropy green fluid, and great prostration. In such cases chromium is found in the urine. Even its external use is attended with danger. One application of about 50 gr. in ½ oz. of water was made to the external genitals of a woman after removal of papillary vegetations. In twenty-seven hours she died in a state of collapse. Congestion of the kidneys and liver was found, and both organs contained chromium.

Toxicology.—Toxic effects have resulted from potassium dichromate, from chromium trioxid, and from lead chromate. As the poisonous properties of lead chromate, *chrome yellow*, are mainly due to the lead contained in it, they are properly considered under the compounds of lead (p. 327).

Symptoms.—When swallowed, the compounds of chromium act as gastro-intestinal irritants, with additional effects upon the central nervous system. They cause a disagreeable taste, vomiting, pain, diarrhea, collapse, unconsciousness, dilated pupils, very slow respirations, and muscular cramps.

Fatal Dose.—Death has occurred in fourteen hours from about 3 dr. of potassium dichromate, while, on the other hand, there has been a case of recovery from 273 gr.

Fatal Period.—Death from 1 oz. has occurred in forty minutes.

Treatment.—Chalk or magnesia should be given to neutralize the acid. Milk may be administered or used to wash out the stomach with the pump or tube. Anodynes are indicated for the pain, cerebral, and respiratory stimulants for the depression of the nervous system.

Postmortem Appearances.—Chromic-acid preparations are absorbed with great rapidity both by stomach and skin, and its elimination is mainly by the kidneys, but to some extent by the liver and bowels. In acute cases death is caused by respiratory arrest or central nervous disturbance. In the gastro-intestinal tract are found inflammation, ecchymoses, and swollen follicles. An early morbid change is parenchymatous nephritis; the spleen is shrunken and the blood altered.

Tests for Chromium Salts.—Soluble chromates yield with *silver nitrate* a red precipitate; with *lead nitrate*, a yellow precipitate; with boiling dilute *sulphuric acid* and *alcohol*, a green color and the odor of aldehyd.

When *hydrogen sulphid* is added to an acid solution of a chromate, sulphur is precipitated and the red color changes to green from the formation of a basic chromium salt of the acid. When ammonium hydroxid is added to this green solution the hydroxid $Cr(OH)_3$ is precipitated as a bluish green jelly.

Ammonium sulphid causes the same green precipitate from a solution of any salt of chromium, such as the chlorid or sulphate.

Detection.—Having treated organic matters with hydrochloric acid and potassium chlorate, the liquid turns green from chromic chlorid. Ammonium hydroxid added to the filtered liquid in slight excess will yield hydrated chromic oxid as a precipitate, which, after washing and drying, can be converted into potassium chromate by fusing with potassium nitrate and carbonate. After dissolving the fused mass (which will be more or less yellow in color if chromium be present) in water and making slightly acid with acetic acid, the chromate can be detected by the tests given above.

ZINC

Symbol, Zn. Atomic weight, 65.37.

Occurrence.—This metal occurs abundantly in nature as carbonate, silicate, and sulphid (*blende*). Reduced by heating with charcoal the free metal distils into receivers from which air is excluded.

Properties.—It is a white, rather soft metal, melting at 410° C. (760° F.), and at a bright-red heat volatilizing and burning. Commercial zinc often contains a trace of arsenic. In either air or water it first oxidizes and later forms a coherent coat of hydroxid and carbonate which protects the metal underneath. This coat does not dissolve in water unless the water contain chlorids. If heated to over 100° C. (212° F.) the brittle metal softens and can be rolled into *sheet zinc* which retains its tenacity at common temperatures. This is the form generally used in the arts. To protect iron sheets, tubes, and implements they are given a coat of zinc. Iron so treated is called *galvanized iron.* This superficial covering of zinc with its hydroxid makes the iron more durable. Zinc is a constituent of brass and German silver.

The Ion of Zinc.—This metal resembles iron, manganese, and chromium in many respects, but, unlike those metals, it has but one valence. Zincion, Zn^{++}, is divalent and white, like magnesion. Owing to the prevalence of the metal in certain soils it is sometimes found in plants, and in consequence, traces are occasionally discovered in plant-fed animal tissues. Zinc has been found in the liver of cadavers under circumstances which precluded the possibility of poisoning, since the clinical history presented no symptoms attributable to the metal deposited.

Zinc Oxid (ZnO) (*Zinci Oxidum, Zinc White*).—By burning the metal in the air the pigment *zinc white* is prepared. As compared with white lead, it is less poisonous and does not darken by hydrogen sulphid, but it has less covering power.

It is a soft white powder, permanent, odorless, tasteless, and insoluble. Dose: 1 to 10 gr. (0.066–0.66 gm.).

Unguentum zinci oxidi contains 20 per cent. zinc oxid.

Zinc hydroxid, $Zn(OH)_2$, is the white precipitate formed when sodium or ammonium hydroxid is added to solutions of zinc salts. A base added in excess redissolves the deposit. In the presence of much alkali, $Zn(HO)_2$ splits off hydrion from the hydroxyl:

$$Zn(OH)_2 = H^+, H^+, (ZnO_2)^=.$$

Hydrion gives it acid properties and a soluble sodium zincate, Na_2-ZnO_2, is formed:

$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O.$$

In the presence of acids containing hydrion it dissociates in a different sense:

$$Zn(OH)_2 = Zn^{++}, 2(OH)^-.$$

All acids combine with the zincion to form the corresponding zinc salt.

Zinc Carbonate ($ZnCO_3$) (*Zinci Carbonas Præcipitatus*).—When solutions of zinc salts are boiled with solution of an alkaline carbonate a white precipitate of a basic carbonate forms, containing hydroxid.

Zinc phosphid (Zn_3P_2) (*zinci phosphidum*) is a gray-black powder formed when phosphorus is thrown upon melted zinc. It is insoluble in water and alcohol. Dose: $\frac{1}{50}$ to $\frac{1}{20}$ gr. (0.0013–0.003 gm.).

Zinc Acetate ($Zn(C_2H_3O_2)_2$, $3H_2O$).—By the action of acetic acid on the metal soft white scales are produced. These are soluble, efflorescent, metallic in taste, with an acetous odor. The aqueous solution, 2 gr. to 1 fl. oz., is used as a local astringent.

Zinc in Food.—Zinc is soluble in the weak acids of foods. The well-known fact that milk keeps sweet longer in zinc vessels than in pots is explained by the neutralization of lactic acid by the zinc, which is taken up as a lactate. Not only may milk thus be contaminated, but also vinegar, soup, olive oil, and alcoholic liquids. The symptoms produced by articles of food thus contaminated are not grave, and the effects of zinc oxid upon those who work in zinc factories are so inconspicuous as hardly to deserve the name of poisonous. The "zinc fever" sometimes seen in workers in brass and other foundries where zinc is vaporized and inhaled is marked by indigestion, headache, colic, diarrhea,

cramps in the legs, and peripheral neuritis, symptoms which might be attributable to the arsenic which is usually present in commercial zinc. Of the small amounts sometimes contained in drinking water stored in galvanized pipes and tanks, without doubt only a minute proportion is absorbed and that is soon eliminated. When larger doses have been taken repeatedly the metal has been found in the liver and as an excretion in the bile of the gall-bladder. As regards toxicity, pure zinc salts are classed with those of copper and not with the slowly cumulative, metallic poisons, arsenic, antimony, mercury, and lead.

Poisonous Salts.—Of 65 cases of acute zinc-poisoning, all were caused by the two soluble salts, the sulphate and the chlorid. The sulphate was to blame in 25 cases, of which 8 were due to mistaking it for "Epsom salt." Zinc chlorid was the poison in 40 cases. The form used in 26 cases was "Burnett's Disinfectant;" in 4 it was "soldering fluid."

Zinc Sulphate ($ZnSO_47H_2O$) (*White Vitriol*).—This salt can be made by the action of sulphuric acid on zinc, or by heating the sulphid in the presence of oxygen:

$$ZnS \quad + \quad 2O_2 \quad = \quad ZnSO_4.$$

It is metallic in taste, freely soluble, and occurs in crystals so closely resembling magnesium sulphate that it is often mistaken for it. The zinc salt is sometimes kept in the household as a prompt emetic for emergencies. "Epsom salt" is also a domestic remedy, and both are often kept in the same closet in loose packages without labels.

These facts account for the frequency with which accidental poisoning occurs. In doses of 20 or 30 gr. zinc sulphate will evacuate the stomach without causing much depression. This effect is so constant that even after doses of 1 oz. are taken recovery is the rule. When complete expulsion does not occur it acts as a gastro-intestinal irritant, causing vomiting, purging, and, secondarily, dangerous prostration. In 1 case there was neither vomiting nor purging, but death occurred in less than four hours from the depressing action on the nervous system.

Zinc chlorid, $ZnCl_2$, is readily formed by dissolving zinc in hydrochloric acid and concentrating the solution by evaporation until it crystallizes. It is a very soluble, deliquescent salt, present in *Burnett's Disinfectant*, also in the embalming fluid used for preserving bodies for dissection. It is a dehydrating agent, condensing and hardening the tissues. When zinc oxid is dissolved in a concentrated solution of zinc chlorid, an *oxychlorid*, $ZnOHCl$, crystallizes in a hard mass. A similar and less irritating *oxyphosphate* forms when the oxid is dissolved in glacial phosphoric

acid. For dental purposes the plastic paste is put into cavities, where it rapidly hardens. It is a valuable cement.

A soldering fluid is made extemporaneously by dissolving zinc to saturation in hydrochloric acid. This fluid is used to cleanse the surface of metals, so that the solder can make a perfect joint. In the shape of fused caustic sticks the chlorid is used to transfix cancerous tumors, the effect being to disorganize the growth for a considerable area, as the salt absorbs water from the tissues and diffuses readily. It is sometimes applied as a paste by cancer quacks in so careless a manner as to cause death. This external application to the breast may produce general symptoms of poisoning by zinc, and the metal be found in the liver and other organs.

Symptoms from Zinc Chlorid.—The gastro-intestinal symptoms are those of a powerful corrosive—a metallic taste with instant burning pain in mouth, throat, and stomach. The act of swallowing is difficult and painful, and the salivary flow excessive. Violent vomiting begins immediately, often of bloody matters; purging supervenes, with tenesmus and bloody stools. Collapse may end in coma and death in a few hours. If life be prolonged, nervous sequelæ are common, such as perversion of the special senses, localized muscular spasms, muscular weakness, and aphonia. The local action may cause stricture of the gullet or pylorus, and also destruction of the glandular structure of the stomach, thus impairing digestion, so that inanition, extreme wasting, and even death may ensue.

Fatal Dose.—The prompt emetic action of zinc sulphate has brought about recovery after doses of 1 oz.; death has ensued from taking 1½ oz. The caustic action of zinc chlorid has caused death secondarily after several weeks from the administration of 6 gr. Recovery has been brought about after a dose of 200 gr.

Fatal Period.—While death has occurred in about four hours from administration of zinc sulphate without vomiting, and in another case from zinc chlorid, yet there are instances of death from the secondary effects of disorganization of the stomach and stricture of the gullet as late as one hundred and sixteen days after the dose.

Treatment.—The efforts of the stomach at evacuation must be assisted by free drafts of warm water or warm milk. The stomach-tube may be used in the very exceptional cases when emesis is not prompt. The antidotes are milk, eggs, and the vegetable astringents containing tannin, represented by strong decoctions of green tea.

Postmortem Appearances.—The usual consequences of irritant poisoning, more or less intense, are to be seen—that is, con-

gestion in the mouth, gullet, stomach, and intestines; areas of softening, ulceration, and even perforation. When death is due to secondary starvation, there is usually narrowing of the gullet, with thickening and corrugation.

Tests for Zinc Salts.—Hydrogen Sulphid Tests.—A stream of this gas precipitates white zinc sulphid from an alkaline or neutral solution, or a solution made acid by acetic acid. This precipitate is soluble in the mineral acids, but insoluble in acetic acid, the alkalis, and the alkaline sulphids.

Ammonium sulphid gives the same precipitate, the only white insoluble sulphid obtained by this procedure.

Potassium ferrocyanid can be used to distinguish zinc sulphate from magnesium sulphate and oxalic acid, both of which have been mistaken for it. White zinc ferrocyanid is thrown down from a solution containing zinc sulphate, but the two others yield no precipitate.

Detection.—Organic matters supposed to contain zinc may be digested at a gentle heat with dilute acetic acid, filtered, the filtrate concentrated, and the metal thrown down as sulphid by a stream of hydrogen sulphid. This precipitate, collected on a filter, is washed, dissolved in strong nitric acid, evaporated to dryness, the residue taken up with water, and precipitated as a hydratocarbonate by adding sodium carbonate and boiling thoroughly. Having filtered and washed the precipitate, it can be dried, ignited, and weighed as ZnO. A small portion of the hydrated carbonate may be fused on platinum with a drop of cobalt nitrate. The zinc is detected by the green color resulting.

NICKEL

Symbol, Ni. Atomic weight, 58.68.

COBALT

Symbol, Co. Atomic weight, 58.97.

These metals belong to the iron group, their sulphids being soluble in acids.

Nickel.—*German silver* is an alloy of nickel, zinc, and copper. Alloys of nickel, 25 per cent., and copper, 75 per cent., are widely used for coins of lower value. For this it is fitted by its hardness, malleability, and resistance to the action of air. Nickel-plating is much used to protect iron from rust. None of the salts of this metal are used in medicine.

The Ion of Nickel.—In its stable compounds the element is present as the divalent nickelion, Ni^{++}, which imparts a green color to solutions containing it.

Cobalt, like iron, melts at a high temperature, becomes coated with oxid in moist air, decomposes water at a red heat, and dissolves in the strong mineral acids. Like iron, also, it forms two

series of salts, in the *cobaltous* occurs the divalent ion, Co^{++}; in the *cobaltic*, the trivalent ion, Co^{+++}. The chief use of cobalt in the arts is to impart a dark-blue color to glass and porcelain by fusion with the silicates.

Tests for Nickel and Cobalt.—*Ammonium sulphid* yields a black precipitate with salts of both metals. *Ammonium hydroxid* causes a deposit of hydroxids, soluble in excess; that of nickel being green, that of cobalt blue. The hydroxids thrown down by potash and soda have similar colors to those caused by ammonium hydroxid, but are not dissolved by excess of the base.

VII.—THE GOLD GROUP

In this group are gold, platinum, and molybdenum, heavy metals whose sulphids are insoluble in water and dilute acids, but soluble in ammonium sulphid.

GOLD (Aurum)

Symbol, Au. Atomic weight, 197.25.

As gold is found free and untarnished in nature, not combining with oxygen of the air at any temperature, it is classed with platinum and silver as a *noble metal.* As a *tellurid* it is found in the combined state.

On account of the high specific gravity of this element (19.3) it can be separated from earth, crushed rock, and sand by mechanical washing. To separate washed gold from impurities it is first treated with mercury, with which it amalgamates, and then, on being distilled, the gold remains in the retort.

When combined, as in the *tellurid*, the cyanid chemical process is used. The finely crushed ore is treated with potassium cyanid, which dissolves out the gold as a double cyanid, *potassium auricyanid*, $KAu(CN)_4$. This salt has potassium as cation, and for anion a group, aurocyanidion. Metallic zinc or electrolysis can be used to set the gold free from the other elements.

Properties.—Gold is a soft metal, orange yellow by reflected light, green by transmitted light and when molten. It melts at 1200° C. (2192° F.) and is a good conductor of heat and electricity. Being very malleable, it can be hammered into a thin translucent *foil*. *Cohesive gold*, used by dentists to fill teeth, is made by heating gold foil to redness, thus restoring a property of cohering lost when the foil was beaten out thin. It resists the chemical action of the strong acids singly, but is dissolved, as stated above, by mercury and the cyanids, and also by chlorin-water,

nitromuriatic acid, alkaline hydroxids, and nitrates. To render it hard enough for daily use it is alloyed with silver and copper. Pure gold is said by the mints to be 1000 fine, by jewelers 24 *carats fine;* if, however, the alloy has only 75 per cent. of gold, it is 18-*carat gold,* the other 6 parts being copper and silver.

The Ions of Gold.—The soluble salts of gold are trivalent, forming the ion Au^{+++}, and are called *auric.* There are other compounds, known as *aurous*, which contain the metal as a monovalent element. When an atom of gold meets the undissociated chlorin of chlorin-water, the electric interaction causes the former to be ionized to a cation and the latter to anions, while the dissociated gold chlorid dissolves.

$$Au + Cl + Cl + Cl = Au^{+++}, Cl^-, Cl^-, Cl^-.$$

This is the third mode of ion formation, consisting in the simultaneous charging of electricity by the contact of dissimilar atoms.

Gold chlorid is prepared by dissolving pure gold in nitromuriatic acid. From this yellow solution, by careful evaporation, yellow crystals are obtained of hydrochloroauric acid, $HAuCl_4$. Stronger heat drives off HCl and leaves soluble, deliquescent, brown crystals of gold trichlorid, $AuCl_3$.

Auri et sodii chloridum, $NaAuCl_4 \cdot 2H_2O$, is an orange-yellow soluble powder prepared from equal parts of gold chlorid and sodium chlorid. It is one of a large series of double salts obtained by the action of the solution of hydrochloroauric acid on salts, especially chlorids. The chlorid of gold and sodium is used in medicine as a tonic, and also in photography as a wash to give a brown-violet tone of reduced gold. Dose: $\frac{1}{30}$ to $\frac{1}{10}$ gr. (0.002–0.006 gm.).

Its *toxic effects* are similar to those of mercuric chlorid—*i. e.*, gastro-enteritis, mental disturbances, and convulsions. The *treatment* is by eggs and other albuminous substances.

Tests.—*Hydrogen sulphid* yields a dark brown precipitate of auric sulphid, Au_2S_3, which is insoluble in acids, but soluble in yellow ammonium sulphid. With *ferrous sulphate* a brown powder is deposited, which when dried and burnished shows the yellow luster of gold. A similar reaction is obtained from other reducing agents, such as sulphurous acid and oxalic acids.

PLATINUM

Symbol, Pt. Atomic weight, 195.

Occurrence.—This valuable element occurs in small quantities in many places. It is found mixed with rarer and little-used metals of the same group called *iridium*, *osmium*, *palladium*, *rhodium*, and *ruthenium.*

Properties.—Platinum is gray and silvery in color, with the very high specific gravity 21.4. It melts with great difficulty and resembles gold in its indifference to the strongest reagents. It is used in the arts and in the laboratory for crucibles, dishes, and stills, resisting chemicals and high direct temperatures better than porcelain. It makes easily fusible alloys with molten metals, and is dissolved by nitrohydrochloric acid and hot alkalis. The acids nitric, sulphuric, hydrochloric, and hydrofluoric have no action upon it, but it unites with free chlorin, and, at a red heat, with phosphorus and sulphur. Its ductility and malleability are shown in the fine wire and thin sheets used in the arts. It has the same co-efficient of expansion as glass, and hence is used to conduct electricity through Edison lamps, into which it fuses without cracking the glass.

When the double chlorid of platinum and ammonium is heated the platinum is set free not as white metal, but as a loose mass called *spongy platinum*. By chemical reduction of platinum compounds a finely divided form is obtained, known as *platinum black*. Enormous quantities of gases (several hundred volumes of oxygen) are absorbed by this fine powder. The reactions of the absorbed gases are accelerated to a pronounced degree; in this way platinum is a catalyzer, causing direct union of hydrogen and oxygen (pp. 87 and 93).

The Ions of Platinum.—The valence of platinum is exhibited in two series of salts, divalent and tetravalent.

Platinochlorids.—When dissolved in nitrohydrochloric acid a yellow solution is obtained, leaving on evaporation crystals of hydrochloroplatinic acid, H_2PtCl_6. This is used as a reagent for precipitating potassium and ammonium from solutions in the form of the difficultly soluble salts K_2PtCl_6, *potassium platinochlorid*, and $(NH_4)_2PtCl_6$, *ammonium platinochlorid*. The corresponding salt of sodium is not precipitated. These are commonly called double chlorids of the metals.

Barium platinocyanid, $BaPt(CN)_4 \cdot 4H_2O$, is prepared by passing hydrocyanic acid into hot water containing platinous chlorid and barium carbonate. Like the other complex platinum compounds with cyanogen, it is derived from the divalent ion $Pt(CN)_4^{=}$. The light yellow crystals are iridescent, with a greenish violet light. *Fluorescent screens* are made from it, which have the power of making ultraviolet rays—radium and uranium radiations and Rontgen rays—visible to the eye (see p. 54).

Tests for Platinum Salts.—With *hydrogen sulphid* platinum solutions yield a dark brown precipitate, insoluble in hydrochloric acid. With *potassium* or *ammonium hydroxid* and excess of hydrochloric acid a yellow precipitate results.

CERIUM

Symbol, Ce. Atomic weight, 140.25.

Cerium is a rare metal of the family of alkaline earths. It forms two series of salts: *cerous*, containing tricerion, Ce^{+++}; and *ceric*, containing tetracerion, Ce^{++++}. In the arts it is of some importance because its oxid, CeO_2, is added in small amounts to thoria to make the brilliant white mantles of incandescent gas lights. Alloyed with iron it is used to "strike a light" against a steel file. The flying particles of cerium keep incandescent long enough to ignite a flame.

Cerii oxalas ($Ce_2(C_2O_4)_3 \cdot 9H_2O$) (*cerium oxalate*) is a white powder, tasteless and odorless, insoluble in water or alcohol. It is used in obstinate vomiting in the form of a pill. Dose: 1 to 5 gr. (0.06–0.66 gm.).

THORIUM

Symbol, Th. Atomic weight, 232.42.

This metal is a constituent of very rare minerals, notably of *monazite sand*. Its oxid, *thoria*, ThO_2, is a white powder which is left as a coherent mantle on firing the cotton netting of a Welsbach light saturated with the nitrate. An addition of about 1 per cent. of cerium oxid is necessary for the most perfect light. This metal shares with uranium and radium radio-active powers, sending out through opaque envelops rays which light up phosphorescent substances, influence photograph plates, and discharge electrified bodies (see p. 248). It is the progenitor of a series of ten radio-active elements that decompose finally into bismuth (A. W. 208). Among these the most valued are mesothorium and thorium emanation (p. 250).

URANIUM

Symbol U. Atomic weight, 238.5.

This metal is rare and of difficult fusibility, having no technical use in the pure state. It forms compounds that appear to be stages in a series in which it is first trivalent and last octavalent. Besides these it forms cations, such as $U(OH)_4^{++}$ and UO_2^{++}, contained in the salts of *uranyl*. *Uranium glass* is a bright yellow with a brilliant green fluorescence. The mineral *pitchblende* has grown famous as the chief source of radium. It is a black substance, composed mainly of uranous uranate, $U(UO_4)_2$.

This mineral or any salt of uranium has the power of acting through an opaque cover upon a photograph plate, just as if light had shone on it exposed. These emissions conduct away the charge of an electrometer, and make luminous a screen of

barium platinocyanid. Like radium, it appears to be an inexhaustible source of radiant energy—chemical, electric, and optic (see p. 248). It is the mother substance, from which are descended by spontaneous disintegration a series of ten radio-active elements, including ionium, radium and niton, and closing with lead (A. W. 207.5). Actinium is one of its progeny, and it in turn breaks down into another series of six radio-active elements.

MOLYBDENUM

Symbol, Mo. Atomic weight, 96.

This is a metal like uranium, with a variety of compounds and with a valency ranging from II. to VI. By roasting its native sulphid, MoS_2, the oxid is formed.

Molybdenum trioxid, MoO_3, is the anhydrid of a series of acids, varying in the proportions of water. The trioxid unites with other acids to form more complex acids, as *phosphomolybdic acid*, $H_3PO_4 . 12MoO_3$, which is a reagent for precipitating alkaloids.

Ammonium molybdate dissolved in nitric acid gives *molybdic acid*, H_2MoO_4, which is used to precipitate phosphoric acid as a yellow powder, the ammonium salt of the above acid. This precipitate is insoluble in acids, but soluble in ammonium hydroxid. From this ammoniacal solution *magnesia mixture* precipitates *ammonium-magnesium phosphate.*

VANADIUM

Symbol, V. Atomic weight, 51.

A triad metal—this is widely diffused in clays and massive rocks. It is silvery white, sp. gr. 5.5, melting at 1720° C. Ferrovanadium is an alloy with iron added to steel to increase its hardness, malleability, and tensile strength. The chlorid is used as a mordant in printing fabrics; the trioxid, V_2O_3, is used in steel making. Vanadiumism is a chronic intoxication due to the absorption of the metal into the system. The symptoms are anemia, dry cough, emaciation, irritation of eyes, nose, and throat, nausea, diarrhea, albuminous urine, and a series of nervous phenomena, such as headache, amaurosis, vertigo, and melancholia. Continued exposure to the poison may cause fatal involvement of the lungs, kidneys, blood, and nervous system. Recovery usually ensues upon absence from the works, but for prevention these should be properly ventilated to carry off fumes and dust, but personal cleanliness of nose, mouth, and hands is also necessary.

ORGANIC AND PHYSIOLOGIC CHEMISTRY

Organic chemistry deals with the products peculiar to organized bodies. These products are not found in nature, except in living organisms. The most characteristic of them have been made by synthesis in the laboratory, and thus it has been established that the same chemical forces are concerned in the production of both organic and inorganic substances. All of them are *carbon compounds in which the carbon is combustible.* As carbonates do not burn, they are considered to be inorganic. Some organic compounds exist in plants ready-made, like sugar, starch, and medicinal alkaloids; some, like urea, albumin, and oils, are found in animals. Many are derived from petroleum, or, like the anilin products and carbolic acid, are made from coal-tar; or, like creosote and wood spirits, result from the distillation of wood. Fermentations of different kinds produce alcohol and acetic acid, which, in turn, yield many derivatives.

Organic analysis may be of different degrees of refinement. *Proximate analysis* may be simply the determination of water and solids by evaporation to dryness in a water-bath, and weighing the residue. The presence of carbon is detected by ignition in a crucible, the residue swelling up, blackening, and taking fire, leaving an incombustible whitish remainder. The part that burns is said to be *organic,* the remainder is stated as *ash.*

A finer division is obtained from the solid residue by washing out the *fats* with ether, the *extractives* with hot alcohol, and the *soluble minerals* with hot water, leaving the *proteins* and *insoluble minerals*. The proteins may be separated into the various *albumins,*—the fats into saponifiable and non-saponifiable, and the minerals into different metallic salts.

Ultimate analysis is performed by breaking down the compound into simpler combustion products with the heat of a Bunsen burner. Qualitative results are obtained by the following procedures:

Experiment 1.—Into a small dry test-tube put a piece of starch. Heat to redness while holding the tube horizontally. The starch swells and blackens and drops of water appear on the cool part of the tube. The water proves the presence of hydrogen, the charring proves that carbon is probably present. To make sure of the carbon it must be burned in a current of air and the product of combustion passed into lime-water. A white precipitate is characteristic of carbon dioxid (p. 103).

Experiment 2.—We can detect nitrogen by causing it to combine with hydrogen as ammonia, NH_3, which is easily identified by its odor and alkalinity. Into a small dry test-tube put some pieces of cheese, glue, quill, wool, or hair with soda-lime. A strip of moist red litmus-paper is held in the upper part of the tube, which is heated in a horizontal position. There is a disagreeable smell, the smoke turns the red paper blue, a dew is seen on the glass, and a charred residue in the bottom of the tube.

Experiment 3.—A nitrogenous organic substance ignited with sodium produces sodium cyanid, NaCN. Into a small dry test-tube put a small quantity of uric acid. Upon it place a piece of sodium, twice the size, and heat in a Bunsen flame until charring occurs and other action ceases. While still hot the tube is stirred about in a test-glass of water, so that the tube breaks and its contents dissolve. The black matter may be allowed to settle or it may be filtered out, and the clear portion be tested for sodium cyanid by the *Prussian-blue test.* Add a few drops of fresh ferrous

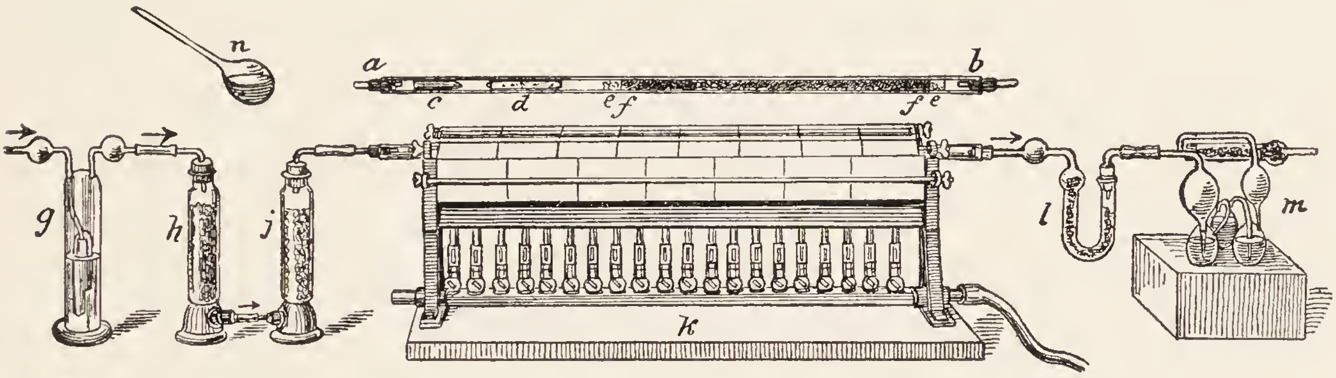


Fig. 71.—Estimation of carbon and hydrogen by combustion of organic substance: *a* to *b*, Combustion tube; *e*, *e*, asbestos plugs; *f* to *f*, copper oxid; *n*, glass bulb for volatile liquid; *d*, platinum boat containing substance analyzed; *l*, drying tube containing calcium chlorid; *m*, potash bulbs; *g*, *h*, *j*, apparatus for ridding air of its moisture and carbon dioxid; *k*, furnace of gas burners.

sulphate, the same quantity of ferric chlorid, and enough hydrochloric acid to change the brown precipitate to a blue solution of ferrous ferrocyanid.

Ultimate analysis reveals how few are the elements that enter into the composition of the great number of organic bodies. Of these few elements cyanogen contains: C and N; the hydrocarbons C and H; the fats and carbohydrates have C, H, and O; the alkaloids C, H, O, and N; albumin has C, H, O, N, and S; nerve matter C, H, O, N, S, and P; hemoglobin C, H, O, N, S, and Fe.

The substance to be analyzed is placed (Fig. 71) with an oxygen-yielding compound, CuO (*f* to *f*), in a hard glass tube (*a* to *b*) plugged loosely with asbestos (*e*, *e*). The tube is then heated in a furnace (*k*), while a stream of oxygen, dried in the towers of calcium chlorid or sulphuric acid (*h*, *j*), carries the combustion to the point of complete oxidation. The carbon is converted into

CO_2, which is caught in the absorption bulbs (m) containing KHO; the hydrogen changes to H_2O, which is absorbed in passing through the tube (l) holding $CaCl_2$. The increase of weight in the absorption bulbs and drying tube stands for the carbon dioxid and water resulting from the combustion. The molecular weight of CO_2 is 44, and for every 44 (11) parts, 12 (3) are carbon. The molecular weight of water is 18, and for every 18 (9) parts 2 (1) are hydrogen. The difference between the sum of the weights and the weight of the body analyzed represents the oxygen which was not collected.

Example.—Let us suppose the analysis to be of a piece of sugar weighing 0.09005 gm. On combustion it forms 0.0539 gm.

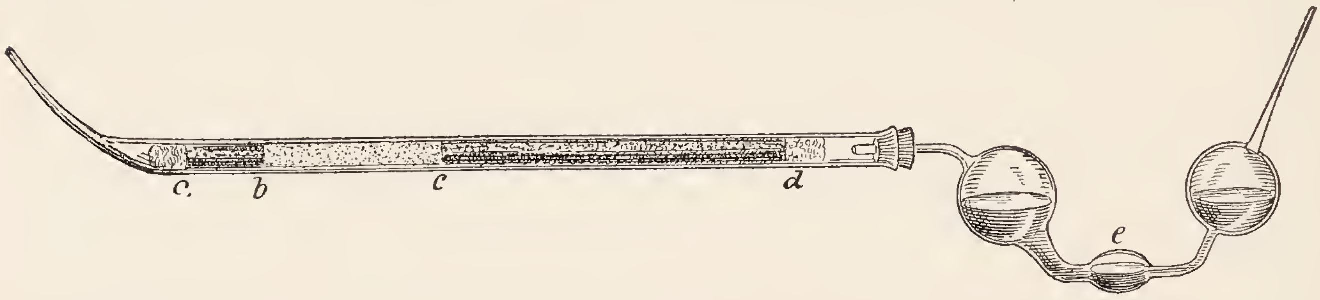


FIG. 72.—Nitrogen estimated as ammonia: *a*, Asbestos wad; *a* to *b*, soda-lime; *b* to *c*, substance tested and soda-lime; *c* to *d*, soda-lime; *d*, asbestos plug; *e*, absorption bulb containing hydrochloric acid.

of H_2O and 0.19005 gm. of CO_2. As $\frac{1}{9}$ of H_2O is hydrogen, the sugar contains $0.0539 \times \frac{1}{9} = 0.00599$ gm. of H. As $\frac{3}{11}$ of CO_2 is carbon, the sugar contains $0.19005 \times \frac{3}{11} = 0.03819$ of C. Therefore, 100 gm. of sugar contains $\frac{100 \times 0.00599}{0.09005} = 6.65$ gm. of hydrogen, and $\frac{100 \times 0.03819}{0.09005} = 42.41$ gm. of carbon. The remainder is oxygen.

$$\text{Then, to state percentage:} \begin{cases} C = 42.41 \\ H = \ \ 6.65; \\ O = 50.94. \end{cases}$$

Nitrogen Content.—If there be reason to believe that *nitrogen* is present, then heating in a furnace with soda-lime (Fig. 72, *a* to *b* and *c* to *d*) gives the N as NH_3 gas. This ammonia is caught by passing into HCl contained in a suitable tube (e), where it is fixed as NH_4Cl. The NH_4Cl is precipitated with platinum chlorid, weighed, and the calculation made on the basis of the molecular weight of NH_4 as 18, and nitrogen, 14.

Kjeldahl's process for estimating the total nitrogen of various nitrogenous bodies is a standard method suitable for organic solids or liquids: (1) By boiling with strong sulphuric acid the nitrogen is converted to ammonium sulphate. (2) Next this acid solution is decomposed by heating with excess of sodium hydroxid. The ammonia gas evolves and is received in an absorbing fluid which is a known volume of standard acid. The diminution of acidity is finally determined volumetrically.

(1) Thus, in testing urine 5 c.c. are treated in a round-bottomed digesting flask of 500 c.c. capacity, with a pinch of yellow mercuric oxid (0.3 gm.) or 0.2 gm. of copper sulphate to assist oxidation and 20 c.c. of pure strong sulphuric acid. To prevent loss from spurting, a piece of paraffin about the size of a pea is added and the flask sloped over a small flame until the mixture boils. At first it blackens. In twenty minutes 10 gm. of ignited potassium sulphate in powder is added to raise the boiling-point and the gentle boiling continued for another forty-five minutes, by which time the black color is discharged. All the nitrogen in the urine is now dissolved as ammonium sulphate.

(2) The cooled acid solution is washed into a liter flask (*a*) for decomposition and diluted to a volume of 300 c.c. Ten pieces of granulated zinc are added to prevent bumping and a bit of paraffin to check frothing; about 1 gm. of sodium thiosulphate is added to liberate nitrogen from mercuric oxid. Sodium hydroxid, 40 per cent., in excess is run in from the tap funnel (*b*), which is drawn out to a fine point below. On heating, the ammonia distils into the absorption flask (*h*) which contains a measured amount (about 30 c.c.) of one-fifth normal sulphuric acid. This acid has a few drops of methyl-orange in it and was poured into flask *h* through the absorption tube (*n*) so as to leave the broken glass in it, wet with the dilute acid, to catch any traces of ammonia which may escape the acid in flask (*h*). The ammonia enters the flask (*h*) by way of a 50-c.c. pipet which dips just below the surface of the acid and by its enlargement (*d*) receives any of the acid sucked back from flask (*h*) and prevents its entering flask (*a*). As soon as all the NaHO solution has dripped slowly in, the cock is closed and the mixture is boiled about a half hour, when about two-thirds have passed over. The methyl-orange must not change to yellow, which would indicate that the acid in (*h*) had not been sufficient. The evolution of ammonia being completed, the absorption tube (*n*) is washed with water and the acid made up with water to 200 c.c. It is then transferred to a beaker and titrated with one-fifth normal sodium hydroxid in a buret. *Example:* Suppose it is found that the neutral point is reached when 20 c.c. of the equivalent soda solution have been added. Then 30 c.c. — 20 c.c. = 10 c.c., which

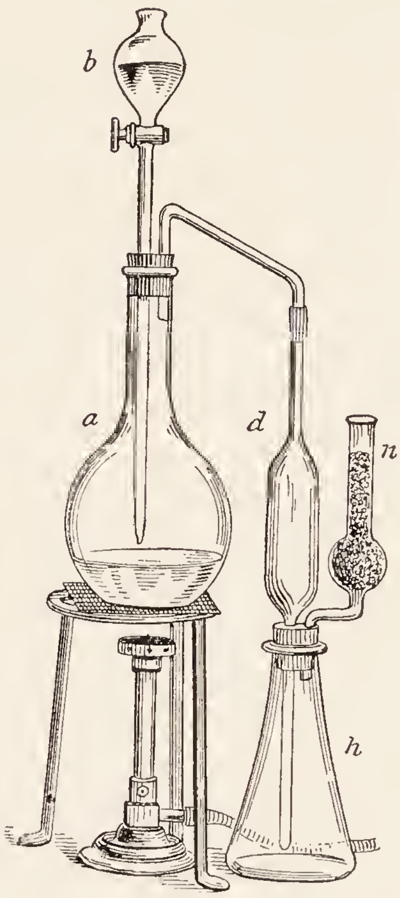


FIG. 73.—Kjeldahl process, apparatus for decomposition of ammonium sulphate.

represents the amount of acid consumed in absorbing the ammonia. As 1 c.c. of one-fifth normal H_2SO_4 corresponds to 0.0028092 gm. of nitrogen this balance of 10 c.c. contains $0.0028092 \times 10 = 0.028092$ of N. As 5 c.c. of urine yields this 0.028092, 100 c.c. would yield $20 \times 0.028092 = 0.561840$ gm. percentage of nitrogen.

Phosphorus and Sulphur Content.—Having removed the carbon and hydrogen by oxidation, the residue containing sulphur and phosphorus is completely oxidized by fusing a known quantity with a mixture of potassium nitrate and sodium carbonate. The P is oxidized to P_2O_5, which is determined by solution and precipitation with magnesia mixture. The S is oxidized to SO_4, which is determined by solution and precipitation with $BaCl_2$.

Empiric Formula.—When it is desired to determine the formula of an organic substance, we first analyze it by the combustion process and calculate the percentage of the constituents. The percentage divided by the atomic weight gives the proportional number of atoms, which proportion can be simplified by dividing each term with a common factor which in the case below is 3.33.

Example.—A sample of acetic acid on combustion yielded carbon, 39.95 per cent.; hydrogen, 6.69 per cent. Then the remainder was oxygen, 53.36 per cent.

$$C = \frac{39.95}{12} = 3.33 \quad \text{or} \quad 1 \text{ as lowest ratio;}$$

$$H = \frac{6.69}{1} = 6.69 \quad \text{or} \quad 2 \quad \text{" \quad "}$$

$$O = \frac{53.36}{16} = 3.33 \quad \text{or} \quad 1 \quad \text{" \quad "}$$

Molecular Formula.—The simplest expression of the ratio of its elements being 1 : 2 : 1, the empiric formula of acetic acid would be CH_2O. But formaldehyd, CH_2O, acetic acid, $C_2H_4O_2$, and lactic acid, $C_3H_6O_3$, all have the same percentage composition, and the same empiric formula. The formula found most useful is one which tells the total number of atoms in the molecule. This *molecular formula* may not express the lowest ratio, but a multiple of it. There are several methods of deducing it, one of these depending on the determination of the vapor density.

The law is that the *molecular weight* is equal to *twice the vapor density* (H = 1) or to the *specific gravity* of its *vapor* (air = 1) *multiplied by* 28.88. The density of the vapor of acetic acid is 30 times that of hydrogen; therefore, its molecular weight is $30 \times 2 = 60$. But the formula CH_2O sums up to a molecular weight of 30; to make it 60 we must double the atoms and write it $C_2H_4O_2$.

As acetic acid is an organic acid, the analysis of one of its salts is of value. For this purpose the salt of silver is preferred, a weighed quantity of which ignited in a porcelain crucible gives a residue of pure silver. Experiment shows that there is but 1 compound of silver with acetic acid, 1 atom of hydrogen being replaced by 1 of silver. As 100 parts of silver acetate leave a residue of 64.68 parts by weight of silver, the vanished portion was 35.32 parts of the C, H, and O. The atomic weight of silver is 107.66; therefore, $\frac{35.32 \times 107.66}{64.68} = 58.8$. In the salt 1 atom of hydrogen of the acid was replaced by 1 of silver and must be restored to get the true molecular weight: $58.8 + 1 = 59.86$; in round number 60. Its formula would therefore be—

$$\begin{array}{lcr} C_2 & = & 24 \\ H_4 & = & 4 \\ O_2 & = & 32 \\ \hline & & 60 \end{array}$$

The **cryoscopic method** for determining molecular weight is serviceable for substances which cannot be vaporized without decomposition. A solution of sugar freezes at a lower temperature than does pure water, the depression of the freezing-point of weak solutions being directly proportional to the weight of sugar dissolved. For example, to dissolve sugar, 1 part in 100 of water, is to depress the freezing-point of the water from 0° C. (32° F.) to −0.058° C. (31.8956° F.); a 2-per cent. solution lowers it to −0.116° C. (31.7912° F.); 3 per cent., −0.174° C. (31.6868° F.). On testing weak solutions of various organic substances in other solvents, such as acetic acid, benzene, etc., it is found that the lowering of the freezing-point is approximately proportional to the number of molecules of the dissolved substance in a given weight of the solvent, irrespective of the nature of the substance.

Law of Raoult.—From these facts Raoult deduced the law *that solutions in a given quantity of the same solvent of the molecular weight in grams of different substances will lower the freezing-point to the same degree.* That is to say, with *normal* solutions (gram molecular) in a given solvent the freezing-point lowering is a constant quantity, called the *co-efficient of molecular depression* and indicated by K. The value of K for water is 19; for acetic acid, 39; for benzene, 49.

To determine the molecular weight of an organic substance dissolve 1 gm. (P) in 100 of the solvent, and observe the depression of the freezing-point (D). Then, molecular weight = $\frac{K \times P}{D}$. The observation is best made with *Beckmann's apparatus*, described under Cryoscopy (p. 38).

Example.—Cane-sugar, 5.139 gm. (P), dissolved in 100 c.c. of water, lowered the freezing-point 0.295° C. (D). The constant for water as solvent (K) is 19; then, $\frac{19 \times 5.139}{0.295} = 331$. This is very near the theoretic value, 342.

The Boiling-point Method.—In another place it has been stated that dissolved substances raise the boiling-point of a solvent to an extent corresponding to the depression they cause in the freezing-point. In both cases the effect depends upon the ratio between the number of molecules of the dissolved substance and the number of those of the solvent. Observations must first be made to fix the boiling-point constant of the solvent. This is done by noting the rise of boiling-point (p) of the solvent occasioned by dissolving in 100 gm. of it, the molecular weight in grams of any non-electrolyte or undissociated solid. The apparatus employed is described below.

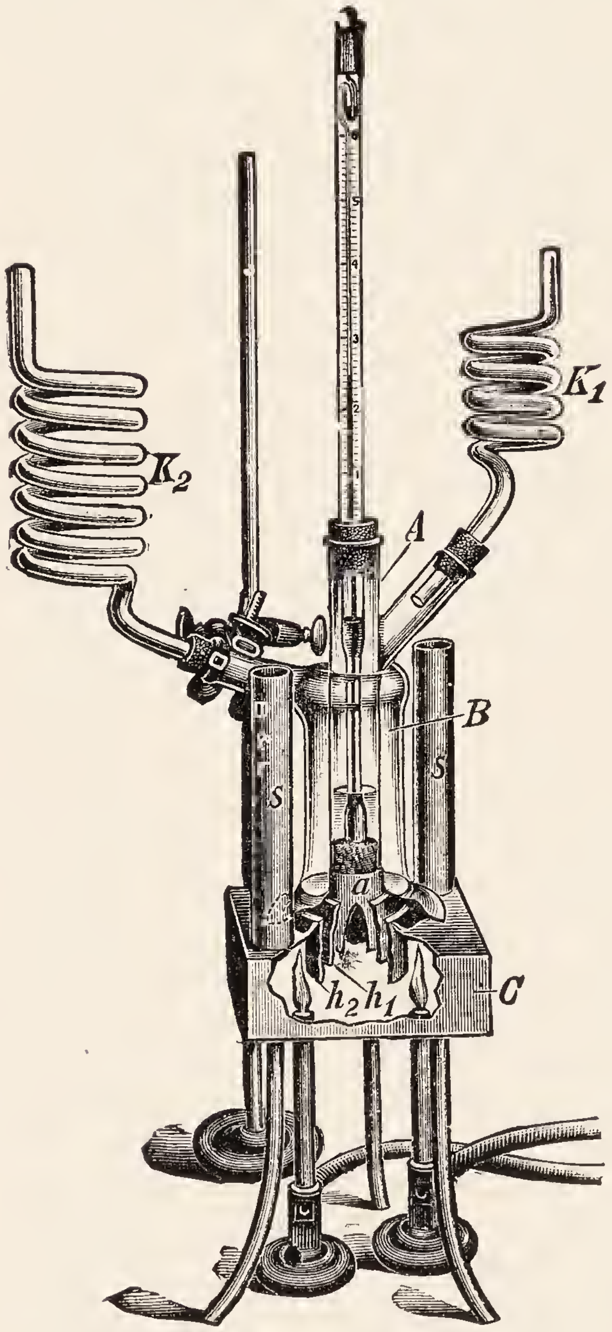


FIG. 74.—Beckmann's boiling-point apparatus.

Beckmann's Method for Determining the Boiling-point.—The effect produced upon the boiling-point of a fluid by dissolving substances in it is determined by the apparatus shown in Fig. 74. The solution to be studied is put in the glass tube, A, so as to cover the bulb of the thermometer. Below the bulb (not touching it) and at the bottom of this tube are glass beads which promote ebullition at a uniform rate. Rising from the boiling tube is a worm-like condenser, K, for returning the vapor. Surrounding the tube, A, is a double-walled glass jacket, B, containing some of the same solution that is being studied in A. Connected with B is a returning condenser, K_2. The apparatus stands on an asbestos box, heated by two burners below.

First, pure water or any other solvent to be used is put in A, with the beads, and boiled. The special thermometer is inserted

and adjusted while in the apparatus, so that the surface of the mercury stands between 0° C. (32° F.) and 1° C. (33.8° F.), after the thermometer has been gently knocked. Heat is withdrawn and the tubes emptied, cleaned, and dried. Again the beads are put in *A* with a weighed amount of the pure water or other solvent. The thermometer is again put in place and the condenser inserted. The glass jacket *B* is also filled with the solvent, and the contents of *A* and *B* are both heated to boiling for twenty minutes. A record is made of the reading of the thermometer and the barometer. Again the heat is withdrawn; a weighed quantity of the substance, the molecular weight of which is to be determined, is dissolved in the solvent contained in *A* and *B*. The lamps are now applied and the liquids boiled, the temperature is taken and corrected for any barometric changes. The record made by the pure solvent subtracted from that of the solution gives the rise due to the substance dissolved. The elevation is proportionate to the quantity dissolved, provided the substance is not volatile.

The molecular weight is determined by the formula $m=\frac{pw}{rs}$, in which w = gram-weight of the substance dissolved; p = the boiling-point constant of the solvent; r = observed rise in boiling-point; s = gram-weight of the solvent. The value of p for water is 5.1; for acetic acid 25.3; for ether 21.6; for ethyl alcohol 11.7.

Effect of Dissociation.—The inorganic electrolytes (acids, bases, and salts) show greater depression of the freezing-point and elevation of the boiling-point than do the organic non-electrolytes. The lowering and the rise are dependent upon the number of particles, which in organic solutions is limited to the molecules dissolved. The quantities increase in value with the inorganic electrolytes, because their molecules are partly dissociated into ions which add to the number of particles in solution.

Constitutional or Structural Formula.—Experiment with bases shows that only 1 of the H atoms in acetic acid, $C_2H_4O_2$, is replaceable by a metal. To express this fact 1 atom may be set apart as $C_2H_3O_2H$. When acted upon by phosphorus terchlorid, 1 atom each of H and O are substituted by a single atom of chlorin. Then to represent this idea of the constitution, the OH must be set apart as in this equation:

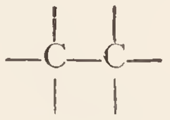
$$3C_2H_3O\,.\,OH \quad + \quad PCl_3 \quad = \quad 3C_2H_3OCl \quad + \quad PO_3H_3.$$

We are justly entitled to assume that the H and O are linked together in the group hydroxyl. Other experiments give sanction to the view that 3 of the hydrogen atoms are contained in a methyl

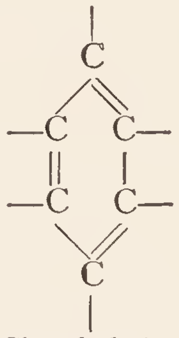
group, CH_3, and this notion, added to the others, is usually represented in the *constitutional* or *rational* formula, $CH_3 . COOH$, which is read, *methyl united with carboxyl.*

Classification of Carbon Compounds.—The starting-point for the study of organic chemistry is the compound consisting only of carbon and hydrogen, and known as a *hydrocarbon.* The other more complex substances may be regarded as derived from hydrocarbons by rearranging the atoms in the molecule, or by substituting for the hydrogen atoms other elements or groups of elements known as *radicals.* These changes are accomplished by the agencies referred to under Inorganic Chemistry, such as heat, oxidation, reduction, the energetic action of the halogens, nitric acid, and caustic alkalis; and by processes called organic, such as the fermentations and putrefactions.

The number of substances to be grouped for study is enormous and their classification by no means easy. One system, not perfect, but which is generally adopted and has the merit of simplicity, is based upon the assumption that all organic substances with constitutions that have been worked out are derivatives of one of two hydrocarbons, methane, CH_4, or benzene, C_6H_6. The two great classes are (1) those closely related to methane, called *paraffins*, *aliphatic* or *fatty compounds*, and (2) those allied to benzene, called the *coal-tar*, *cyclic*, or *aromatic compounds.* In the paraffins the carbon atoms are linked in an *open* or *arborescent chain.* The aromatic compounds contain one or more *closed chains* or *rings.*



Open chain.



Closed chain.

In both classes are found compounds, the nature of which is indicated in the following summary:

(1) *Hydrocarbons* containing only hydrogen and carbon, as marsh gas, CH_4.

(2) *Halogen derivatives*, or *halids*, in which one or more halogen atoms are substituted for the hydrogen of a hydrocarbon, as methyl chlorid, CH_3Cl.

(3) *Alcohols*, the hydroxids of hydrocarbon radicals, as ethyl alcohol, C_2H_5OH.

(4) *Aldehyds*, compounds of a hydrocarbon radical and the group COH; for example, acetic aldehyd, $CH_3 . COH$.

(5) *Acids*, compounds in which hydrocarbon radicals are united to carboxyl, COOH, as acetic acid, $CH_3 . COOH$.

(6) *Ethers*, combinations of two hydrocarbon radicals with oxygen, as ethyl ether, $(C_2H_5)_2O$ or $(C_2H_5) . O . (C_2H_5)$.

(7) *Compound ethers* or *esters*, compounds formed like mineral salts by replacing the hydroxyl in an alcohol with an acid radical:

$$\underset{\text{Ethyl alcohol.}}{C_2H_5OH} + \underset{\text{Acetic acid.}}{CH_3CO_2H} = \underset{\text{Acetic ether.}}{C_2H_5CH_3CO_2} + H_2O.$$

(8) *Ketones*, compounds of two hydrocarbon radicals with carbonyl, as dimethyl-ketone or acetone, $CH_3 . CO . CH_3$.

(9) Derivatives not classified in the above summary, such as:

Carbohydrates, originally so called because they contain carbon joined to hydrogen and oxygen, which are combined in the same ratio as in water, thus: glucose is $C_6H_{12}O_6$. They are regarded as being aldehyd alcohols or ketone alcohols, as when glucose is written $CH_2OH(CHOH)_4CHO$.

Amins and *amids*, compounds in which the hydrogen of ammonia, NH_3, has been replaced by basic and acid radicals respectively, as ethylamin, $NH_2C_2H_5$, and acetamid, $NH_2C_2H_3O$.

Proteins, compounds of carbon, hydrogen, oxygen, nitrogen, sulphur, and sometimes phosphorus or iron. They are complex and indefinite in structure, as albumin, fibrin, and casein.

ALIPHATIC COMPOUNDS

Methane (CH_4) (*Marsh Gas*).—This is the simplest member of a numerous series. Its common name, *marsh gas*, is due to its occurrence in the gases which bubble up on stirring the decaying vegetable matter at the bottom of stagnant pools. Another name, *fire-damp*, is given it by coal miners who encounter it escaping from fissures in the coal veins. It is the chief component of the natural gas of petroleum districts of Pennsylvania, Ohio, and Indiana, and of the illuminating gas manufactured by the distillation of bituminous coal. It is formed when steam with vapor of carbon bisulphid is passed over heated copper:

$$CS_2 + 2H_2O + 6Cu = CH_4 + 2Cu_2S + 2CuO.$$

This is an illustration of synthesis or building up of an organic compound from the elements, as CS_2 and H_2O are easily made from carbon, sulphur, hydrogen, and oxygen.

Methane is prepared by heating in a hard glass tube 1 part of anhydrous sodium acetate with 4 parts of soda lime.

$$\begin{array}{ccccccc} CH_3CO_2Na & + & NaOH & = & CH_4 & + & Na_2CO_3 \\ \text{Sodium acetate.} & & \text{Sodium hydroxid.} & & & & \text{Sodium carbonate.} \end{array}$$

In this reaction acetic acid is broken up, as most carbon acids are, by heat, yielding a hydrocarbon and a carbonate.

Experiment.—The sodium acetate is first made anhydrous by heating it in a porcelain capsule until it fuses to a brown liquid. It must be stirred to prevent spurting. The cooled residue is ground with the soda-lime and introduced into a test-tube. The tube, fitted with a delivery tube by a cork, is held horizontally while being heated. The burner is kept moving to prevent melting the glass tube. The gas is collected over water in other tubes. If a tubeful inverted is closed with the thumb and held mouth down, the gas stays in the tube and may be tested with a taper as hydrogen is sometimes tested. The gas burns at the mouth; the taper goes out as it is passed up inside the tube (Pl. 1).

Properties.—It is a colorless, odorless gas, slightly soluble in water, over which, however, it can be collected. It does not support combustion, and causes suffocation when breathed. It burns with a non-luminous flame, and mixed in the proportion of 1–5 with air forms a highly explosive mixture. Accidents in coal-mines are frequent from the *fire-damp*. Before the mixture in air reaches the explosive ratio the presence of the gas is detected by the blue flame or *corpse light* inside the miner's safety lamp (p. 103).

$$\begin{array}{ccccccccc} CH_4 & + & 2O_2 & = & CO_2 & + & 2H_2O \\ \text{2 volumes} & + & \text{4 volumes} & = & \text{2 volumes} & + & \text{4 volumes.} \end{array}$$

A very marked trait is its stability, being unaffected by some of the most energetic chemical agents. It is equally unaffected and undissolved when passed through bromin in the dark, the caustic alkalis, strong acids, and the oxidizers, potassium permanganate and chromic acid. Other hydrocarbons of the same class resist reagents in the same way, having feeble chemical energies; hence they are called paraffins—*slight affinity.*

To express the constitution of methane and the valency of each atom in its molecule, the following diagram is used, based upon the tetravalence of carbon and the univalence of hydrogen:

$$\begin{array}{ccc} & H & \\ & | & \\ H— & C & —H \\ & | & \\ & H & \end{array}$$

Ethane, C_2H_6, is a constituent of the natural gas of petroleum districts, and is dissolved in the crude petroleum. It is produced when methyl iodid is treated with sodium in a neutral medium:

$$\underset{\text{Methyl iodid.}}{2CH_3I} + 2Na = \underset{\text{Ethane.}}{C_2H_6} + 2NaI.$$

To show that ethane may be regarded as containing two methyl groups, this reaction is written—

$$\left.\begin{matrix} CH_3I \\ CH_3I \end{matrix}\right\} + \left\{\begin{matrix} Na \\ Na \end{matrix}\right\} = 2NaI + \begin{matrix} CH_3 \\ | \\ CH_3. \end{matrix}$$

This reaction illustrates a very common method of building a more complex compound from simpler parts. It has been shown how methane is formed by synthesis from its elements. Methane treated with a halogen, such as chlorin or iodin, forms methyl chlorid or iodid, which is one step toward the next highest hydrocarbon, ethane. The final step is to remove the halogen by its affinity for a metal, thus permitting the residues to unite. A similar process enables us to pass on to higher members of the same series.

Experiment.—Fill a voltameter with a saturated solution of potassium acetate $(CH_3CO_2)'K^{\cdot}$, containing some potassium hydroxid for absorption of CO_2. The electric current causes the cation K to decompose water, liberating hydrogen at the negative pole, while at the positive pole acetanion breaks up into CO_2, absorbed by the potash, and CH_3, which combines with another CH_3 to form ethane, C_2H_6.

$$\left.\begin{matrix} CH_3CO_2K \\ CH_3CO_2K \end{matrix}\right\} = C_2H_6 + 2CO_2 + K_2.$$

Properties.—Ethane is a colorless, tasteless gas, insoluble in water. It burns with a feebly luminous flame, and mixed with air in the right proportions is explosive. Like methane, it is very stable even when in contact with acids, alkalis, and oxidizers.

The structure of ethane is indicated in the *graphic formula*—

$$\begin{matrix} & H & & H & \\ & | & & | & \\ H- & C & - & C & -H \\ & | & & | & \\ & H & & H & \end{matrix}$$

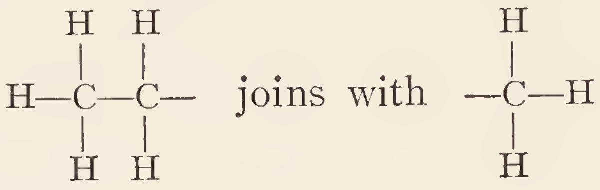
This is deduced from the fact that univalent hydrogen cannot link the two carbon atoms, but carbon, being quadrivalent, can join the other carbon atom and leave six points for the six hydrogen atoms.

Propane, C_3H_8, occurs in petroleum and can be made by treating ethyl and methyl iodids with sodium:

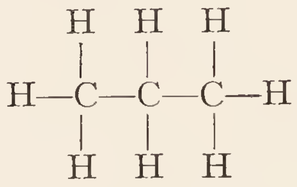
$$\underset{\text{Ethyl iodid.}}{C_2H_5I} + \underset{\text{Methyl iodid.}}{CH_3I} + \underset{\text{Sodium.}}{2Na} = \underset{\text{Propane.}}{C_3H_8} + 2NaI.$$

Properties.—At common temperatures propane is a gas, but below $-17°$ C. (1.4° F. it condenses to a colorless liquid. It burns with a more luminous flame than either ethane or methane, because of the increased proportion of carbon. In its chemical properties it closely resembles the other two hydrocarbons.

From the reaction given above it is concluded that propane is formed by the junction of the ethyl group (C_2H_5) to the methyl (CH_3). Thus:



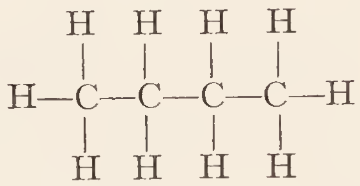
which would give it the constitution—



This may be written $CH_3 . CH_2 . CH_3$ or $CH_3 . C_2H_5$.

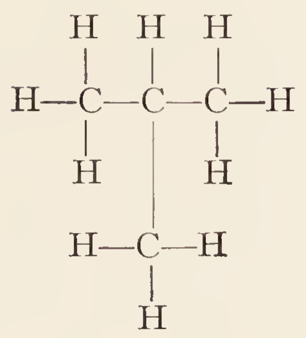
Butane, *hexane*, and a number of other hydrocarbons are found in petroleum, all having chemical properties similar to those of methane.

Butane, C_4H_{10}.—There are two hydrocarbons of this formula. The one occurring in petroleum is often called *normal butane*. From its reactions it is considered to be diethyl, and may be written $C_2H_5 . C_2H_5$, or $CH_3 . CH_2 . CH_2 . CH_3$; the graphic formula being written thus:



The other butane, called *isobutane*, does not occur in petroleum, and differs from the normal butane by being produced in different reactions and having different physical properties. All these hydrocarbons are alike chemically, but this is without doubt distinct from normal butane, though its molecular formula is the same, C_4H_{10}.

A study of its methods of formation and chemical behavior leads to the conclusion that isobutane has the constitution $CH(CH_3)_3$, or, graphically represented:



Isomerism.—The two butanes are called *isomeric* because with the same molecular formula they have different properties. They are said to be *isomers*. By reference to the graphic formulas given above it is plain that isomerism can be explained by a difference in the arrangement of the atoms. When the hydrocarbons are represented in this way there is always found an agreement between the number of isomers and the number of different diagrams it is possible to construct from the molecular formula, assuming carbon to be tetravalent and the carbon atoms to have the power of joining to other carbon atoms to make a skeleton or *open chain*. As the number of carbon atoms increases in the hydrocarbons heavier than butane, the number of possible isomers increases according to the law of permutation. There are three pentanes, nine heptanes, seventy-five decanes, etc.

It has been shown that by similar processes of formation, starting with methane and substituting CH_3 for one atom of hydrogen, we could pass to ethane, from ethane to propane, from propane to butane, etc. Theoretically, there is no limit to the number of hydrocarbons that can be thus constructed, and as a matter of fact those up to C_{40} and over are known and have been separated from petroleum. For these reasons it is convenient to class them together and arrange them in a series beginning with CH_4, and following with other members according to the numbers of carbon atoms. The number of isomers are indicated by the figures in parentheses:

SATURATED HYDROCARBONS

PARAFFINS OR METHANE SERIES

Methane	(1)	molecular weight	16	CH_4	
					difference CH_2
Ethane	(1)	" "	30	C_2H_6	
					" CH_2
Propane	(1)	" "	44	C_3H_8	
					" CH_2
Butane	(2)	" "	58	C_4H_{10}	
					" CH_2
Pentane	(3)	" "	72	C_5H_{12}	
					" CH_2
Hexane	(5)	" "	86	C_6H_{14}	
					" CH_2
Heptane	(9)	" "	100	C_7H_{16}	

Homologous Series.—This series is said to be homologous, because the members are alike in constitution and chemical behavior; because with increase in molecular weight there is a regular and gradual progression in density, boiling-point, and other physical properties; and because consecutive members differ by CH_2. The corresponding derivatives—alcohols, ethers, acids, etc.—may likewise be arranged in well-marked homologous series of similar compounds, differing consecutively by CH_2.

General Properties of Paraffins.—In any homologous series the composition of all the members can be expressed by a molecular formula in general terms. For the paraffins the general formula is C_nH_{2n+2}, the coefficient n standing for the number of carbon atoms. From this general formula the molecular composition of any number can be known. For example, in the fourth member the value of n must be 4, and $2n+2=10$; thus, C_4H_{10}.

There being a similarity in modes of production and chemical properties, it suffices to state the general properties of a series as illustrated in a few members. What is said about these types will apply with small allowances to every member of the series. Hence, a detailed account of each is unnecessary, and for lack of space will not be attempted in this work. To know the behavior of a few common or simple members is to have a basis for understanding all the remainder.

Nomenclature.—It will have been observed that all the names of the methane series terminate in *ane*. From and including the fifth member the prefix is a Greek numeral denoting the number of carbon atoms, as *pent*-ane, *hex*-ane, *dec*-ane, *dodec*-ane. On removing a hydrogen atom there is left a residue or univalent *radical* which is designated by changing the termination *ane* to *yl*, as meth-*yl*, pent-*yl*, etc. When the hydrogen of ethane, C_2H_6, is reduced by 2 atoms there is left a bivalent radical which changes *ane* to *ene*, as C_2H_4 eth-*ene*; reduced by 3 atoms it leaves a trivalent radical, changing the final *e* of *ene* to *yl*, as C_2H_3 ethen-yl.

The *derivatives of the bivalent radicals* are denoted by the ending *ylene*, as eth-*ylene* chlorid, $C_2H_4Cl_2$ (p. 382).

Physical Properties of Paraffins.—At ordinary temperatures the first four members of this series are colorless gases; at lower temperatures, under pressure, they condense to liquids, with a readiness proportionate to the number of carbon atoms. The members from the fourth to the sixteenth are colorless liquids with boiling-points and molecular weights rising together. Above the sixteenth ($C_{16}H_{34}$) the hydrocarbons are colorless solids, the melting-point rising as the series is ascended. They are all insoluble in water, but soluble in alcohol and ether.

Chemical Properties of Paraffins.—They are all saturated compounds and therefore do not unite directly with any element. Their most marked trait is stability, resisting equally well strong acids, alkalis, and oxidizing agents. In sunlight chlorin and, less readily, bromin break them up, substituting halogen atoms for hydrogen.

Petroleum and Natural Gas.—These are the chief sources of the paraffins. In western Pennsylvania and many other parts of the earth a gas issues from the earth under pressure, spontaneously or when wells are bored to certain depths. This gas contains hydrogen, methane, ethane, propane, and other gaseous hydrocarbons. It is probably the product of the decomposition of remains of fish and other sea animals deposited with certain geologic strata.

Another natural product of the same animal destruction in the rocks is *petroleum* or *rock oil*, which escapes into borings from cavities or gravelly strata under the pressure of gaseous constituents.

Preparation.—*Crude petroleum* is a thick, yellowish or brown liquid, lighter than water, which is freed from extraneous organic matter and hydrocarbons other than paraffins by treatment with concentrated sulphuric acid. The acid is removed and the residue of oil treated with alkali. Thus purified, Pennsylvania oil is composed almost entirely of hydrocarbons of the methane series. This crude mixture has some of the gaseous members dissolved in it which make it too inflammable for use in lamps. To get the various gaseous, liquid, and solid components in suitable forms, it is necessary to separate them into mixtures of different boiling-points. The crude oil is distilled from large iron boilers, and the vapors condensed into receivers which are regularly changed as the temperature is made to rise from point to point.

Fractional Distillation.—The saturated hydrocarbons are not decomposed by boiling, and hence may be separated and purified like other volatile organic substances by distilling in fractions. This operation is performed in the apparatus shown in Fig. 75. The organic mixture is placed in the flask *A*, which has a perforated stopper carrying a thermometer, the bulb of which comes just below the side opening, *B*. This side tube connects with a condenser for fluids of low boiling-point, but when the temperature must be raised above 125° C. (257° F.) the strain of hot vapor upon the cold tube of the condenser cracks it. In such cases connection is made with a single long tube, *C*, without an envelop of cold water.

On applying heat the more volatile constituents boil first and are condensed into a receiver. By means of the thermometer

the temperature can be noted and regulated. With the same source of heat the temperature of an organic mixture slowly and continuously rises, and the portions passing over at different intervals of 5° or 10° or of 25° C. are separated by being received in different vessels.

Treated on this principle petroleum yields the commercial products *rhigolin*, b.-p. 21° C. (69.8° F.); *petroleum ether* or *benzin*, b.-p. 50°–60° C. (122°–140° F.); *gasolin* or *naphtha*, b.-p. 75° C. (167° F.); *ligroin*, b.-p. 80°–120° C. (176°–248° F.);

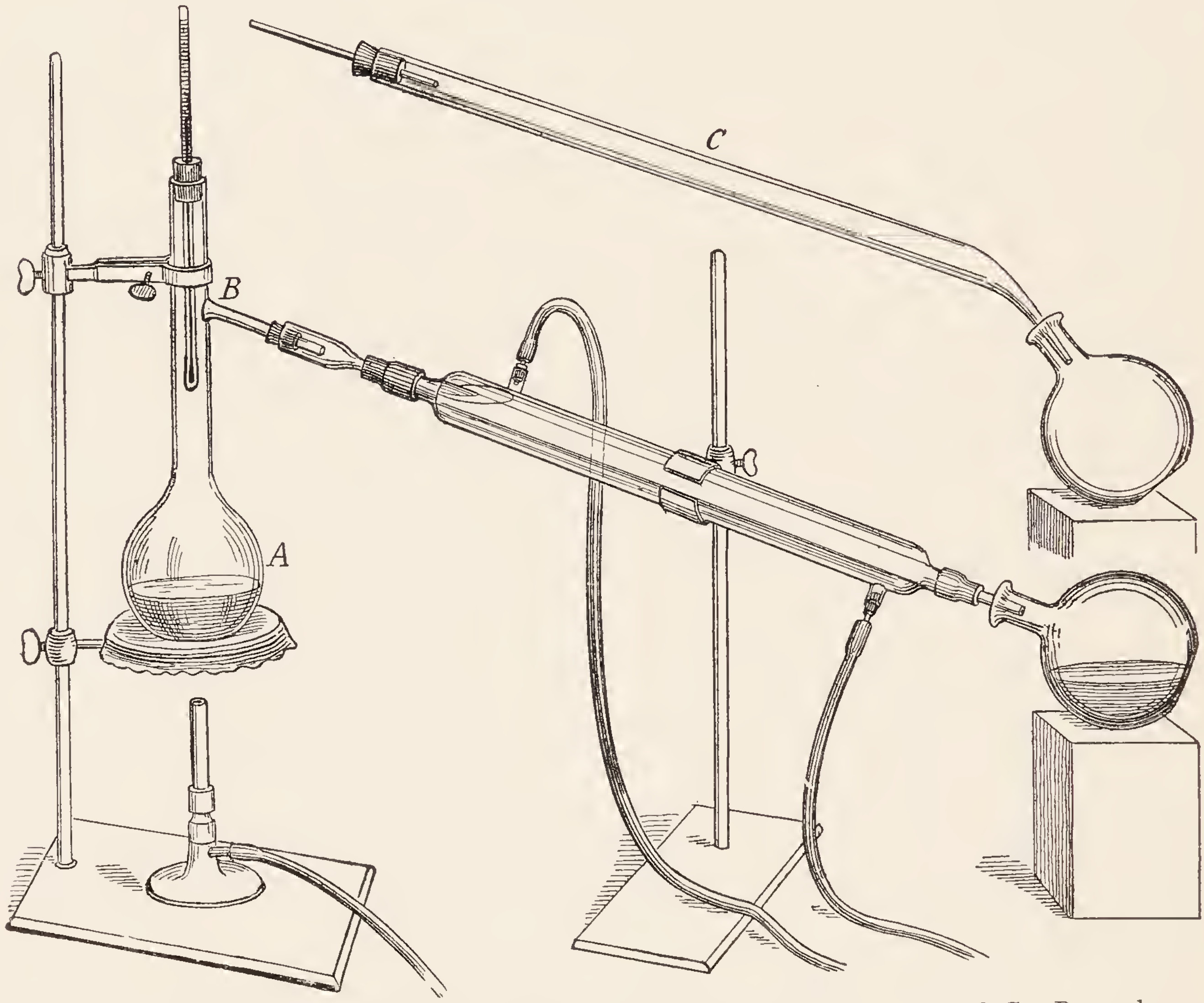


FIG. 75.—Apparatus for distillation: *C*, Condenser without water jacket for 130° C.; *B*, condenser with water jacket for lower temperature.

kerosene or *astral oil* for illumination, b.-p. 150°–250° C. (300°–480° F.); *paraffin oil* or *mineral oil*, b.-p. 250°–300° C. (482°–572° F.); *lubricating oil*, b.-p. above 300° C. (572° F.). The residue, purified by boneblack, is the soft solid, *vaselin* or *petrolatum*, melting at 40°–50° C. (104°–122° F.); and at a higher melting-point, 50°–75° C. (122°–167° F.), *paraffin* or *mineral wax*. *Fuel oil* is a cheap product not used for illumination, but valuable for heating and used for spraying marshes to kill mosquitoes.

Flashing-point of Burning Oils.—Owing to the explosive mixtures made by the gases escaping from the lighter products, the laws prohibit the sale of burning oils which give off inflammable

vapor at temperatures lower than the standard, usually 48° C. (120° F.). Official inspectors test the oil by the *flashing test*, the basis of which consists in the gradual heating of the oil, in which the bulb of a thermometer is immersed so as to determine the point at which a flame will cause a flash due to ignition of surface vapors.

Toxicology.—Petroleum and its products are all somewhat poisonous, the gases by inhalation, the liquids and solids by swallowing.

Symptoms.—In the oil refineries and in rubber factories using benzin as a solvent for rubber, inhalation causes the following symptoms: general debility, palpitation of the heart, staring eyes, hallucinations, cough, chronic bronchitis. *Naphtha drunk* is the name given to the intoxication it produces. This is sometimes induced purposely by inhaling gasolin. In the early stage of this condition the victims may be excited and in high spirits. These symptoms are due to benzin; but the asphyxia is due to the deficiency of oxygen. Symptoms of intoxication have followed the spilling of petroleum in a tenanted room. In very severe cases—cardiac weakness, insensibility, and convulsions may be forerunners of death. When swallowed, petroleum is a local irritant to the stomach, causing pain, vomiting, colic, diarrhea, etc. After absorption it produces headache, dizziness, rapid pulse, labored breathing, cyanosis, drowsiness, collapse, insensibility. Workers in petroleum are liable to boils and a disseminated acne, chiefly on the arms and thighs.

Fatal Dose.—A death is reported from ½ oz. of benzin; on the other hand, recovery has followed from taking 1 pt. of petroleum. Fatal cases are very rare.

Treatment.—The stomach should be evacuated by emetics or by hypodermic injection of 5 drops of a 2-per cent. solution of apomorphin; or by the stomach-tube. Purgatives are used to empty the bowels. For the collapse hot applications, strychnin, and other cardiac stimulants.

Postmortem appearances show no characteristic lesion. The odor of petroleum products should be detected in the contents of the stomach and bowels.

Detection.—The characteristic odor will be noticed in the suspected material and in the vapors obtained by fractional distillation. The distillate will reveal the form of product by inflammability, boiling-point, etc.

UNSATURATED HYDROCARBONS

OLEFIN SERIES

(The possible isomerids shown by numbers in parentheses.)

(1) Ethene or Ethylene, C_2H_4, or $\begin{array}{l}CH_2\\ \|\\ CH_2.\end{array}$

(1) Propene or Propylene, C_3H_6, or $\begin{array}{l}CHCH_3\\ \|\\ CH_2.\end{array}$

(3) Butene or Butylene, C_4H_8, or $\begin{array}{l}CHCH_2CH_3\\ \|\\ CH_2.\end{array}$

(5) Pentene or Amylene, C_5H_{10}, or $\begin{array}{l}CH(CH_2)_2CH_3\\ \|\\ CH_2.\end{array}$

The action of chlorin and bromin upon the paraffins is to produce substitution products, such as ethyl bromid and chlorid. By heating these with alcoholic solution of potassium hydroxid a new sort of hydrocarbon is formed by the loss of 2 hydrogen atoms:

$$\underset{\text{Ethyl chlorid.}}{C_2H_5Cl} + KOH = \underset{\text{Ethene or ethylene.}}{C_2H_4} + KCl + H_2O.$$

Any higher hydrocarbon of the methane series will substitute 1 atom of hydrogen for chlorin, and then with the alkali yield the corresponding ethene hydrocarbon.

The paraffin with 2 carbon atoms is ethane, C_2H_6, a completely saturated compound; but ethene has 2 atoms less of hydrogen, and under certain circumstances can take up this hydrogen again; hence it is called unsaturated. Arranged with other hydrocarbons formed by a similar reaction, there is made a homologous series of the general formula, C_nH_{2n}.

Nomenclature.—The termination *-ene* or *-ylene* is substituted for the *ane* of the corresponding paraffin. There is no methene or methylene, ethene being the simplest member. With chlorin, ethylene forms an oily liquid, *ethylene dichlorid;* hence it was called *oil making* or *olefiant.* From this word is derived the name of the series *olefin.*

General Properties.—Not being saturated, the members of this series are unlike the paraffins, combining directly with other compounds or elements, and forming saturated additive products. The reactions of these hydrocarbons leave no room to doubt that their form of unsaturation is properly indicated by the relation of the carbon atoms in the structural formula for C_2H_4, as $\begin{array}{l}CH_2\\ \|\\ CH_2.\end{array}$

The first four of the series are gases; the fourteen or more above these are liquids; the highest members are solids, showing an elevation in melting- and boiling-points as we pass up the series. Insoluble in water, they dissolve slightly in alcohol. They burn in air with a bright but smoky flame. Mixed in the right proportion with air they can be exploded.

Ethene (*ethylene, olefiant gas*) occurs as a colorless constituent of illuminating gas, to which it imparts the luminous quality not given by methane.

Preparation.—Beside the mode of formation (p. 383) from ethyl chlorid and potassium hydroxid, ethene is prepared by destructive distillation of coal and many organic substances. Compressed in cylinders, it furnishes the gas used in the Pintsch system. By direct union it yields the halogen derivatives, ethylene chlorid, $C_2H_4Cl_2$; ethylene bromid, $C_2H_4Br_2$; and ethylene iodid, $C_2H_4I_2$.

Propene is methyl ethene, $C_2H_3-CH_3$.

Butene is dimethyl ethene, $C_2H_2(CH_3)_2$; or ethyl ethene, $C_2H_3-C_2H_5$.

Pentene (*amylene*) has been produced in three isomers, only one of which is important. This is called *pental, iso-amylene,* or *trimethyl-ethene,* C_5H_{10} or $C_2H(CH_3)_3$. It is prepared by dehydrating amylene hydrate with acids. It is a colorless inflammable liquid. Pental is used in medicine as an anesthetic in doses of 2 or 3 fl. dr. (7.50–11.25 c.c.).

ACETYLENE SERIES

Ethine or Acetylene, C_2H_2, or $\begin{array}{l} C—H \\ ||| \\ C—H \end{array}$

Propine or Allylene, C_3H_4 or $C_2H.CH_3$ $\begin{array}{l} C—CH_3 \\ ||| \\ C—H. \end{array}$

General Properties.—They are unsaturated hydrocarbons of the general formula C_nH_{2n-2}, and are formed by treating the halogen monosubstitution products of the olefins with alcoholic potassium hydroxid:

$$C_2H_3Br + KOH = C_2H_2 + KBr + H_2O.$$

Being unsaturated, they can unite directly with 4 atoms of chlorin or bromin, or with 2 molecules of hydrochloric acid, to form additive compounds. The formula of acetylene expressive of this fact has this structure: $\begin{array}{l} CH \\ ||| \\ CH. \end{array}$

Up to the member $C_{12}H_{22}$ they are gases or volatile liquids of a characteristic odor. Sparingly soluble in water, readily in alcohol, they are inflammable with a luminous but smoky flame.

Acetylene (C_2H_2) (*Ethine*).—The simplest of this series is acetylene, a constituent of coal-gas, and formed when the vapor of methane or coal-gas is passed through red-hot tubes. It has four atoms of hydrogen less than ethane C_2H_6. In the following manner it is a step in the synthesis of alcohol from its elements:

In the presence of hydrogen the arc light between carbon electrodes produces it by a simple synthesis:

$$C_2 \quad + \quad H_2 \quad = \quad C_2H_2.$$

By nascent hydrogen it is raised to C_2H_4, ethylene, and this, by the action of sulphuric acid and water, produces ethyl alcohol, $C_2H_5 . OH$.

Preparation.—The most convenient method, and the one used industrially, is that consisting in the treatment of calcium carbid with water. A gaseous acetylene is evolved and calcium hydroxid remains:

$$C_2Ca \quad + \quad 2H_2O \quad = \quad C_2H_2 \quad + \quad CaH_2O_2.$$

Experiment.—If a piece of calcium carbid is dropped into some water in a capsule, gas bubbles arise which take fire when touched with a lighted match.

Properties.—Acetylene is a colorless gas, odorless when pure, but when impure has an odor resembling garlic. Readily soluble in alcohol, it is but feebly so in water. It liquefies under 48 atmospheres of pressure at 0° C. (32° F.). It burns with a brilliant flame, and from a special jet it gives a light more intense than that of any other gas. Heated by a red-hot surface without air, its 3 molecules change to the polymeric substance, benzene, C_6H_6, which accounts for the presence of benzene in coal-tar. When mixed with the proper proportion of air it ignites with a violent explosion. By cold and pressure it condenses to a very light liquid with a high coefficient of expansion. This is classed by some governments among the dangerous explosives.

Detection.—This depends upon the fact that when passed into a solution of cuprous chlorid in ammonia it forms a brownish, amorphous *copper acetylid*, $C_2H_2Cu_2O$; and the dry powder explodes by percussion or by heat. When absorbed by water the acetylene solution precipitates *ammoniosilver nitrate* a white color; or *ammoniocuprous chlorid*, red. It is not poisonous, as a contaminant of the air, in amounts likely to be inhaled.

HALOGEN DERIVATIVES OF METHANE

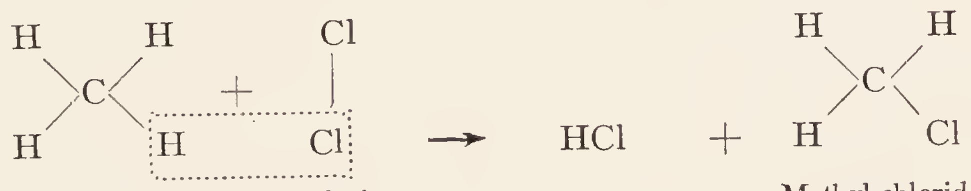
THE methane series forms *halids* with iodin, chlorin, and bromin. Under the influence of daylight upon a mixture of methane and chlorin the following compounds are successively obtained and hydrochloric acid formed:

Methyl chlorid	CH_3Cl	S. G.	0.952 ..	B. P.	—23.7° C.	(—10.66° F.).
Methylene chlorid	CH_2Cl_2	"	1.377 ..	"	+41.6° C.	(106.88° F.).
Chloroform	$CHCl_3$	"	1.526 ..	"	61.2° C.	(142.6° F.).
Tetrachlormethane	CCl_4	"	1.632 ..	"	76.7° C.	(170.06° F.).

The reactions for the first two are indicated in the following equations:

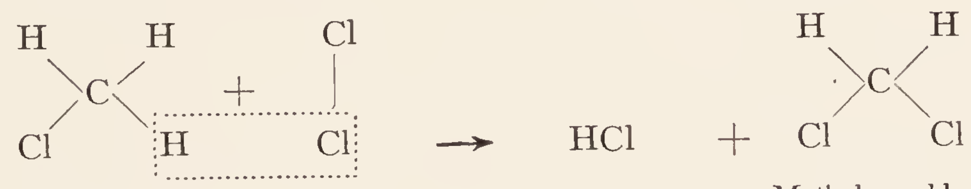
$$(1)\quad CH_4 + Cl_2 = CH_3Cl + HCl.$$
$$(2)\quad CH_3Cl + Cl_2 = CH_2Cl_2 + HCl.$$

To indicate that these are not additive compounds the following graphic equations are used:



Methane. Chlorin. Methyl chlorid.

Another molecule of chlorin acting upon the methyl chlorid carries the change one step further. Thus:



Methyl chlorid. Methylene chlorid.

Substitution.—To produce the other two derivatives requires the same process of extracting hydrogen and replacing it by chlorin, step by step. This process is called *substitution.* It is very general in the case of organic compounds; indeed, a system of classifying them is based upon the notion that all organic substances can be formed from one another by substitution. This process differs from that of salt formation, where the hydrogen of an acid is replaced by a metal. All the hydrogen of the hydrocarbons can be substituted, but this cannot be done with the hydrogen of all inorganic acids, a few of which, such as phosphorous and hypophosphorous acids have some hydrogen that resists

substitution by a metal. The organic hydrogen can be replaced by all sorts of elements and groups, while that of acids only by metals or metal-like compounds. These substitution products are not dissociable like the mineral salts, though some organic acids, bases, and salts behave in the same way as the inorganic compounds.

General Properties.—The table of chlorids shows that the halogen derivatives of the hydrocarbons increase in density and boiling-point progressively with the proportion of chlorin, bromin, or iodin. None of them is a salt; none of them conducts electricity. They are sparingly soluble and their solutions do not give the reaction of the ions of chlorin and bromin with silver nitrate.

Radicals.—In the above list we start with methane, CH_4; hence the substitution products are sometimes named as though they were species of methane. Thus CH_3Cl is chlormethane; CH_2Cl_2, dichlormethane; $CHCl_3$, trichlormethane; and CCl_4, tetrachlormethane. They are sometimes considered to be chlorids of the groups CH_3, CH_2, CH, and the element C. The C takes 4 atoms of chlorin, which accords with the recognized tetravalence of carbon. In all these compounds this valence is evident. The group $CH\equiv$ combines with 3, and hence is trivalent; $CH_2=$ with 2, divalent; and CH_3- with 1, monovalent. These groups do not exist in the free state, but when combined as above hold together through many changes and reactions, with evidences of persistent identity. These methane *radicals* are named as follows: CH_3, *methyl;* CH_2, *methylene;* CH, *methenyl.* The monovalent groups, such as methyl, ethyl, propyl, etc., are called *alkyl*, or alcoholic radicals, and they are often indicated by the letter R. The name *alkylene* is given to the divalent radicals, such as methylene, ethylene, propylene, etc. Other radicals of a different order are the monovalent hydroxyl, $-OH$; carboxyl, $-COOH$; cyanogen, $-CN$; acetyl, $-COCH_3$, and the divalent carbonyl, $=CO$.

Methyl chlorid, CH_3Cl (*monochlormethane*), is a colorless gas of sweetish odor and taste, inflammable, burning with a greenish flame. Liquefied by pressure, it is applied locally for neuralgia, producing intense cold by its evaporation.

Methylene bichlorid, CH_2Cl_2 (*dichlormethane*), an ethereal fluid, is an effective anesthetic, but dangerous, as it paralyzes the heart.

Carbon tetrachlorid, CCl_3 (*tetrachlormethane*), is a volatile liquid extinguishing fires, and a suffocating anesthetic. As "carbona" it is used to clean grease from clothing.

Chloroform ($CHCl_3$) (*Trichlormethane*).—The most important of the halogen derivatives of methane are the trisubstitution products: *chloroform*, *iodoform*, *bromoform.*

Preparation.—The method of obtaining chloroform by direct action of chlorin on methane in sunlight (p. 385) is not convenient nor economic. It is prepared by distilling, over a water-bath, ethyl alcohol or acetone with calx chlorinata, in a large flask fitted to a condenser. Chloroform and water distil over and separate by difference of density, chloroform being one and one-half times heavier than water.

The reaction with alcohol is complex, that with acetone is as follows:

$$\underset{\text{Acetone.}}{2C_3H_6O} + 6CaOCl_2 = \underset{\text{Chloroform.}}{2CHCl_3} + 2Ca(HO)_2 + \underset{\text{Calcium acetate.}}{Ca(C_2H_3O_2)_2} + 3CaCl_2.$$

Properties.—Chloroform is a colorless volatile liquid with a sweetish taste and characteristic odor. Its specific gravity is 1.491. It is neutral in reaction, sparingly soluble in water, dissolving in 5 volumes of alcohol, and mixes in all proportions with ether, benzin, and oils. It does not flash at ordinary temperatures, but burns at very high temperatures with a green flame. It boils at 62° C. (143.6° F.). Mixed with a little air, in a bottle, and exposed to diffused daylight, it decomposes easily; to prevent this it is best kept in amber-colored bottles or opaque containers. It keeps better when 1 per cent. of alcohol is added.

When used for inhalation near an exposed flame the same dangerous irritant products of decomposition are formed as when kept for a long time exposed to daylight:

$$\underset{\text{Chloroform.}}{CHCl_3} \quad + \quad O \quad = \quad \underset{\text{Carbonyl chlorid.}}{COCl_2} \quad + \quad HCl.$$

This carbonyl chlorid, or *phosgene gas*, may be the cause of fatal poisoning.

Chloroformum venale, is the commercial article, which contains sundry hydrocarbons, free chlorin, aldehyd, and hydrochloric acid. These enhance the toxicity and render it unfit for inhalation.

Chloroformum, U. S. P., is purified for inhalation and contains about 1 per cent. of alcohol. Dose, internally: 2 to 20 ♏ (0.12–1.25 c.c.); when inhaled: 1 fl. dr. (3.75 c.c.), repeated.

Tests for Impurities.—A lower specific gravity than 1.47 indicates too much alcohol. After shaking with one-half volume of water, separate and test the water with litmus-paper. If red, then hydrochloric acid is present—confirmed with silver nitrate, which precipitates white with chlorin and hydrochloric acid. Mix and shake frequently with an equal volume of pure sulphuric acid and set aside for one hour. If the acid separate with a brown color, then organic impurities are present. Shaken with potassium hydroxid, it turns brown if aldehyd be present.

Aqua chloroformi, U. S. P., is a saturated aqueous solution. Dose: 4 fl. dr. (16 c.c.).

Spiritus chloroformi, U. S. P., is the alcoholic solution containing 6 per cent of chloroform. Dose 30 ♏ (2 c.c.).

Emulsum chloroformi, U. S. P., contains 4 per cent. of chloroform suspended in a mucilage of tragacanth and oil of almond.

Linimentum chloroformi, U. S. P., contains chloroform, 30 parts, and soap liniment, 70 parts.

Symptoms.—The irritant action is shown by the pain in the throat and stomach, with or without vomiting. The symptoms of gastro-enteritis are soon marked. Some of the vapor is inhaled and the liquid itself is quickly absorbed, inducing the neurotic symptoms. These may be ushered in by a short period of excitement, or may begin at once with the characteristic stupor. The vomiting soon ceases; the breathing becomes irregular and snoring; the pulse thready; the pupils either dilated or contracted; the skin clammy and livid. If the patient recover from the coma, the abdominal pain again becomes urgent. This is often attended by diarrhea and jaundice.

Treatment.—The stomach should be emptied by the siphon tube or by vomiting induced with hypodermic injections of 3 to 5 min. of a 2 per cent. solution of apomorphin hydrochlorid. For a draught and to wash out the stomach, the best antidote is a solution of a tablespoonful of sodium bicarbonate to a tumblerful of water. The failing heart must be stimulated with hypodermic injections of 2 or 3 drops of a fresh 2-per cent. solution of strychnin nitrate. The chest may be flicked strongly at intervals with a wet towel, alternating with hot applications to the chest and abdomen. Electricity and artificial respiration are called for when the respiration is suspended. After recovery from coma the symptoms of gastro-enteritis must be treated as they arise.

Fatal Dose.—By the stomach the smallest fatal dose is 1 fl. dr., given to a boy four years old. For an adult the least quantity swallowed that has killed is about ½ fl. oz. Recovery has followed when the dose was as much as 4 fl. oz.

Fatal Period.—Usually death is delayed for twelve hours, though it has occurred within three hours.

Toxicology when Inhaled as Vapor.—Given as an anesthetic in surgical practice, chloroform has caused many deaths. Statistics warrant the estimate that 1 case out of 3000 inhalations will probably be fatal. It is difficult, but not impossible, to administer chloroform to a person in very deep natural sleep. The odor usually arouses before a stupefying quantity has been inhaled. It takes between five and ten minutes in time, and between 3 and 4 fl. dr. in 1-dr. doses to produce insensibility.

Symptoms.—After a short period of excitement there follows one of lowered activity of the brain and later of the spinal cord. Sensation is lost early and the muscles are completely relaxed. Breathing is affected in the third stage and the heart's action is depressed. The temperature declines, the skin becomes livid, and if the anesthesia be prolonged, death may ensue from failure of respiration or cessation of the heart's activity. Some fatalities are traceable to the cases being obviously unfit from old age, heart disease, diabetes, Bright's disease, and alcoholism. It is dangerous to give chloroform in quantities greater than 1 fl. dr. or undiluted with air. The blood quickly absorbs it, and the centers that actuate and control breathing and the heart's action are paralyzed. Vomiting often occurs and the matter may choke the larynx.

Fatal Dose.—This depends on the concentration. Death has ensued when only 15 drops were inhaled without air. It is hardly safe to give it in a stronger proportion than 4 parts in 100 of air. On the other hand, recovery has been brought about after the inhalation of 20 oz. properly diluted, and the administration distributed over twelve or more hours.

It is dangerous to use chloroform by the open flame of a candle or gas burner. Its vapor is burned into the irritating and suffocative fumes, carbonyl chlorid (p. 387) and hydrochloric acid (p. 387). If the operation and inhalation are prolonged, the patient, the physician, and nurses may all show signs of poisoning, such as cyanosis, difficult breathing, cough, collapse, and even death some hours after.

Treatment.—When the breathing or the pulse suddenly declines there is need of artificial respiration with oxygen inhalation. The head should be lowered, the tongue drawn forward, and strychnin given hypodermically.

Tests for Chloroform.—(1) A drop of chloroform added to a mixture of 1 drop of anilin and alcoholic potassium hydroxid and gently warmed develops a nauseous smell of *isobenzonitril:*

$$CHCl_3 + \underset{\text{Anilin.}}{C_6H_5NH_2} + 3KOH = \underset{\text{Isobenzonitril.}}{C_6H_5NC} + 3KCl + 3H_2O.$$

A distinctly offensive odor can be perceived when the chloroform is present, 1 : 5000.

Fallacies.—The same reaction can be obtained from iodoform, bromoform, chloral, and trichloracetic acid.

(2) A reagent is made by mixing 0.3 gm. of resorcinol in 3 c.c. of water and 3 drops of 10 per cent. sodium hydroxid. When this is boiled strongly with 1 drop of chloroform it becomes yellowish red, with a beautiful greenish fluorescence.

(3) Having dissolved about 0.01 gm. of beta-naphthol in strong potassium hydroxid and warmed it, add the chloroform. A blue color results, changing to green and brown.

(4) *Ragsky Test.*—When death is supposed to have been due to inhalation of chloroform, the lungs should be cut up finely and mixed with a small quantity of water. A flask is provided with a cork, perforated to admit a funnel tube passing to the bottom, and a short delivery tube at the top (Fig. 76). The lung mixture, made alkaline with sodium carbonate to fix volatile acids and free chlorin, is heated in the flask over a water-bath. The delivery tube is connected with a larger hard glass tube, about 18 in. long, which must be heated to bright redness through 4 in. of its length by

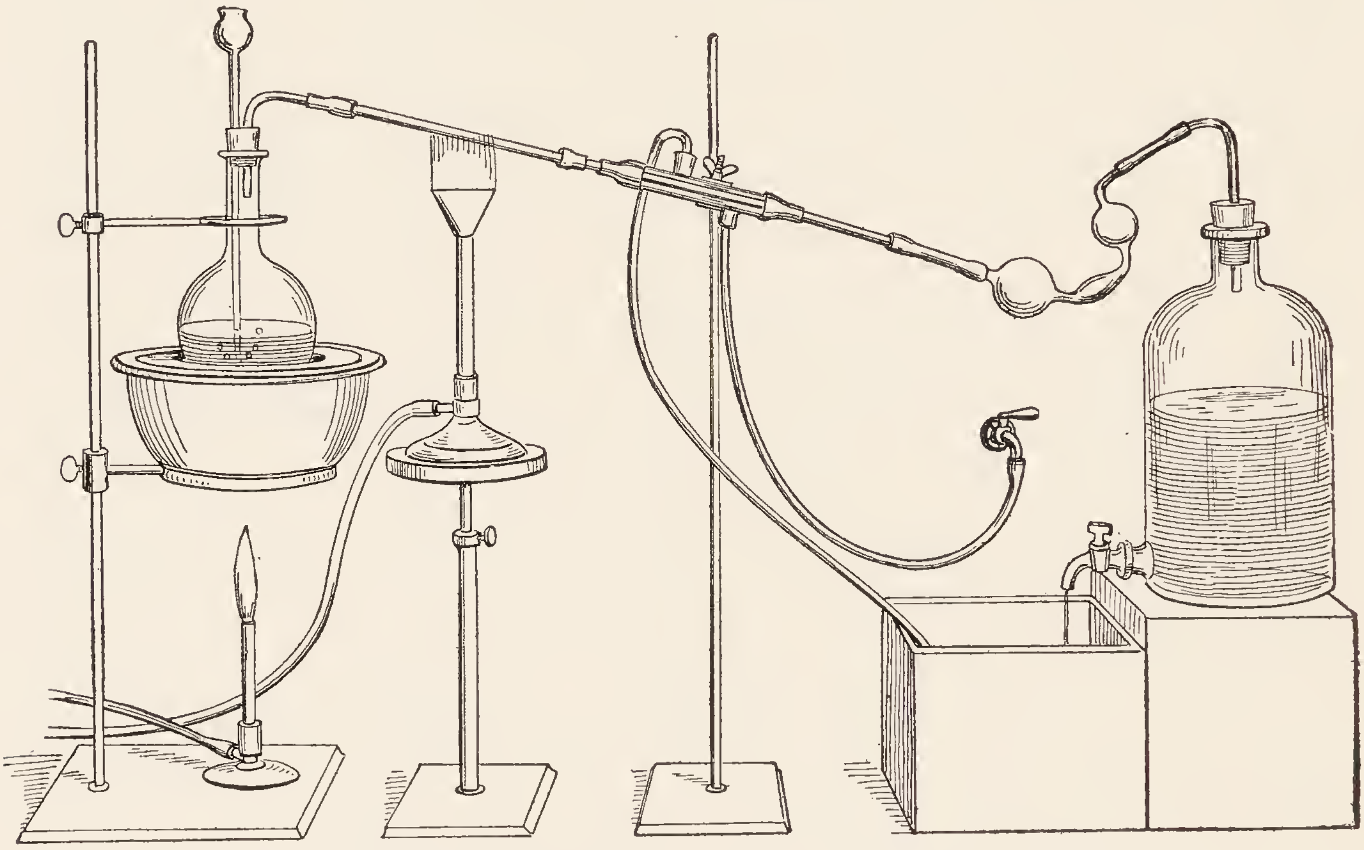


FIG. 76.—Apparatus for detecting chloroform by the Ragsky process.

a broad-flamed Bunsen burner. About 4 in. further along the tube is cooled by a condenser or by wetting a piece of muslin, 1 in. wide, wound about the tube. In the tube, beyond the muslin, is placed a moist piece of iodized starch test-paper. The end of the tube connects with Geissler's bulbs or a wash bottle containing silver nitrate solution, and the exit tube of the bottle is connected with an aspirator. The flask is heated, and, after the tube is red hot, air is drawn slowly through the whole apparatus by the aspirator. It carries air and chloroform to the hot tube, where the vapor decomposes into perchlorbenzene, hydrochloric acid, and chlorin, according to the following reaction:

$$6CHCl_3 = C_6Cl_6 + 6HCl + 6Cl.$$

The perchlorbenzene is deposited as needles in the cold tube, the chlorin liberates iodin from potassium iodid, turning the paper blue, and the hydrochloric acid precipitates the silver nitrate.

(5) *Fehling's solution*, when boiled, is reduced by chloroform to red cuprous oxid.

Iodoform (CHI_3) (*tri-iodomethane*) is closely related to chloroform, chemically. It is formed when ethyl alcohol, aldehyd, acetone, and some other organic substances are warmed with iodin and potassium hydroxid or carbonate:

$$\underset{\text{Alcohol.}}{C_2H_5OH} + 4I_2 + 6KOH = CHI_3 + \underset{\text{Potassium formate.}}{HKCO_2} + 5KI + 5H_2O.$$

Experiment.—A few drops of alcohol are added to a small quantity of 5-per cent. solution of sodium carbonate, and the mixture warmed. Iodin (Lugol's solution), added gradually, causes the separation of iodoform.

Properties.—It is precipitated in the above experiment as lustrous yellowish crystals in the form of six-sided plates having a disagreeable odor of saffron and an unpleasant taste of iodin. It melts at 119° C. (246.2° F.), sublimes readily, and is volatile at ordinary temperatures. It is insoluble in water, but soluble in alcohol and ether.

Toxicology.—Iodoform is extensively used in surgical dressings because of its antiseptic and local anesthetic powers. Used too freely, it has been absorbed with poisonous results. Some of this action is due to iodin set free in the wounds and appearing later in the urine and saliva.

Symptoms.—In certain persons excessive use of iodoform dressings has produced local irritant effects about the wound, marked by redness, pain, swelling, diffused eruptions, inflamed lymphatics, and even death. The systemic phenomena are mainly cerebral; they are malaise, nausea, wakefulness, giddiness, headache, depression of spirits, melancholic delusions, delirium, coma, collapse, and death. Occasionally the type is different, the group of symptoms being drowsiness, stupor, and collapse.

Fatal Dose.—Taken internally, 30 gr. have caused death, though recovery has followed a dose of 120 gr. It is not regarded as safe to apply more than 1 dr. at a time to a wound or absorbing surface.

Fatal Period.—Death may follow after several days' illness, or life may be prolonged for weeks.

Treatment.—The first indication is to clear out the wound, but the gravest symptoms may continue, notwithstanding removal of the iodoform. The nervous phenomena must be treated accord-

ing to their nature. Hypodermic injections of normal salt solution are of benefit.

Postmortem Appearances.—Acute inflammation of the kidneys and pulmonary edema have been found, but most commonly there is fatty change in the kidneys, heart, and liver.

Detection.—Mixed with an alcoholic solution of potassium hydroxid and kept warm for a while, iodoform yields free iodin after acidifying with nitric acid. The very characteristic odor may lead to prompt detection. If this be not perceived, the suspected matter is digested in water, made alkaline, and distilled. The distillate is again made alkaline, agitated with ether, and the ethereal extract evaporated, leaving six-sided lemon-yellow tablets and stars.

Bromoform ($CHBr_3$) (*tribrom-methane*) is formed by a reaction like that of preparing chloroform (p. 387), using the action of alkali hypobromites on alcohol or acetone.

Properties.—It is a colorless, heavy liquid with a sweetish odor and taste, like that of chloroform. By exposure it turns dark from liberation of bromin. It is scarcely soluble in water, but soluble in alcohol and ether.

Toxicology.—Bromoform is used in medical practice as an antispasmodic and sedative in the treatment of whooping-cough. *Dose*, for a child: 2 to 5 drops (0.12–0.3 c.c.) in dilute alcohol or emulsions. After a dose of 15 ♏ a child of four years became unconscious, with contracted pupils, labored breathing, and livid complexion. The child recovered after evacuation of the stomach and stimulation by warmth, electricity, and coffee.

HALOGEN DERIVATIVES OF ETHANE

Ethyl chlorid (C_2H_5Cl) (*chlorethane*) is formed by the action of sunlight on a mixture of ethane and chlorin; or by the action of phosphorus pentachlorid on ethyl alcohol:

$$\underset{\text{Ethyl alcohol.}}{C_2H_5OH} + \underset{\text{Phosphorus pentachlorid.}}{PCl_5} = C_2H_5Cl + \underset{\text{Phosphorus oxychlorid.}}{POCl_3} + HCl.$$

Ethyl chlorid is a gas at ordinary temperature. Under pressure it becomes a colorless, very volatile liquid, boiling at 12.5° C. (55° F.). It is soluble in ether and alcohol, but only sparingly so in water. It does not precipitate silver nitrate in aqueous solution, as it has no chlorin ions, but when warmed with an alcoholic solution of silver nitrate it throws out silver chlorid. Heated with

water or potash, under pressure, it yields ethyl alcohol. Compressed as a liquid in tubes, the vapor is expelled through a small opening, to play upon painful parts as a local anesthetic or inhaled as a general anesthetic. It is highly inflammable.

Ethyl Bromid (C_2H_5Br) (*Bromethane, Hydrobromic Ether*).—This compound can be formed by the same reactions as ethyl chlorid, substituting bromin for chlorin. It is a colorless, heavy, volatile liquid, with a burning taste and a pleasant smell, like that of chloroform. It is miscible with alcohol, ether, and chloroform. It behaves like ethyl chlorid with water, potash, and silver nitrate. Exposed to light and air it turns yellow and decomposes, as chloroform does, into dangerous compounds. When inhaled it causes rapid anesthesia with quick recovery.

Dose, for inhalation, 2 to 3 fl. dr. (7.50–11.25 c.c.); by the mouth, 5 to 10 drops on sugar. It is not a safe anesthetic, as death has happened once in about 4000 cases. It has occurred in less than a minute; but, on the other hand, has been delayed for days. Ethyl bromid boils at 39° C. (102.2° F.), and so easily breaks up by the heat that isolation by distillation is extremely difficult. The disubstitution compound, $C_2H_4Br_2$, *ethylene bromid*, has been given for it by mistake. This is more depressing to the heart, and therefore more poisonous.

Ethyl Iodid (C_2H_5I) (*Iodethane, Hydriodic Ether*).—This is a clear, pleasant-smelling, neutral liquid, which rapidly turns brown when exposed to light and air, liberating iodin. Chemically, it resembles the chlorid and bromid. Insoluble in water, it dissolves in alcohol and ether. It is given by the stomach in doses of 5 to 16 min. (0.3–1 c.c.), as an antispasmodic. Inhaled, 10 to 20 drops at a time, it allays bronchial irritation. It must be given with caution, for it depresses the heart in excessive doses.

OXYGEN DERIVATIVES

Alcohols, Ethers, Aldehyds, Acids

ALCOHOLS

Methyl Alcohol (CH_3OH) (*Wood Spirit, Wood Naphtha*).—The name *alcohol* was formerly sacred to the *spirit of wine*, the volatile and stimulating essence of intoxicating beverages. Chemists having concluded that it was a *compound of the radical hydroxyl*, HO, *with a hydrocarbon radical*, the name was extended to other compounds of like composition, classing them as *the alcohols*.

To distinguish organic hydroxids the syllable "-ol" is used as a suffix. Thus: *methanol* for methyl alcohol, *ethanol* for ethyl alcohol.

When dry wood is heated in retorts and the distilled vapors are condensed, among the volatile products is found methyl alcohol. By fractional distillation it is separated from the creosote and acetic acid that were mixed with it. It is a thin, colorless liquid, with a faint aromatic odor and a burning taste. Its specific gravity is 0.796; boiling-point 66° C. (150.8° F.); freely soluble in water. It burns with a non-luminous flame and without soot; it is used in spirit lamps for heating chafing-dishes, coffee-urns, etc. It dissolves shellac and other resins, and is used to make varnishes. For these purposes commercial forms are found in the shops, named *Colonial spirits*, *Columbian spirits*.

Methylated spirit is a mixture used in the arts under the name "denatured alcohol," free under the excise law because the ethyl or common alcohol is rendered undrinkable by 10 per cent. of methyl alcohol with a trace of benzin. Pure methyl alcohol has been substituted by druggists for ethyl alcohol in preparing essences of cinnamon, ginger, peppermint, lemon, cologne, and bay rum. In certain States where the sale of alcoholic beverages is prohibited it is a common custom to drink these essences and cologne spirits for the ethyl alcohol they should contain when properly prepared.

The **physiologic action** of methyl alcohol differs from that of ethyl alcohol in that the coma persists for longer periods. While in the body it is oxidized to formic acid, which is eliminated as sodium formate, $NaCO_2H$, a stronger poison than the alcohol. It is formed and excreted so slowly that small repeated doses overlap each other with a cumulative effect.

Symptoms.—Its exhilarating effect is quickly followed by vertigo, nausea, vomiting, headache, dilated pupils, delirium, persistent coma, and death. Should recovery take place, there is danger or more or less *blindness*, due to atrophy of the optic nerve.

Methyl alcohol is so poisonous that its domestic use should be abandoned and "*denatured* alcohol" be accepted as a substitute for it. All retail packages of it should bear the "poison" label.

Fatal Dose.—Blindness has followed the taking of 5 teaspoonfuls of methyl alcohol. Something less than ½ pt. has proved fatal.

Fatal Period.—Death may occur in a few hours or be delayed two days.

Treatment.—With the siphon tube the gastric contents should be diluted with warm water and the stomach emptied. Alternations of hot and cold affusions may help the coma. Artificial respiration may be called for, and the circulation need stimulation with strychnin. The optic neuritis will be benefited by strychnin and stimulants.

Test.—Warmed with potassium dichromate and sulphuric acid, the methyl alcohol is oxidized to formic acid. This is separated by neutralizing the sulphuric acid with calcium carbonate and precipitating the chromate with lead acetate. Filtered, the clear filtrate is tested for formic acid by warming it with ammonio-nitrate of silver. A silver mirror is formed on the glass.

Constitution of Alcohols.—It has been stated above that alcohols are believed to be the hydroxids of hydrocarbon radicals. The proof of this structure rests upon certain reactions in which the alcohols behave like metallic hydroxids. On mixing hydrochloric acid with methyl alcohol there is no immediate change. After a time, however, new chemical combinations arise in a manner similar to those attending the interaction of a metallic hydroxid and an acid. Thus:

$$\underset{\text{Methyl alcohol.}}{CH_4O} + HCl = \underset{\text{Methyl chlorid.}}{CH_3Cl} + H_2O.$$

This recalls the reaction of a hydroxid base and an acid forming a salt and water:

$$KOH + HCl = KCl + H_2O.$$

The complete oxidation of methane by combustion is as follows:

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

Intermediate oxidation products (its alcohol, aldehyd, and acid) may be obtained by regulating the conditions. An alcohol is the first stage derived by introducing 1 atom of O into the hydrocarbon. Thus:

$$\underset{\text{Methane.}}{\begin{array}{c} H \\ | \\ H—C—H \\ | \\ H \end{array}} + O \longrightarrow \underset{\text{Methyl alcohol.}}{\begin{array}{c} H \\ | \\ H—C—O—H \\ | \\ H \end{array}}$$

The alcohol is no longer inert, like the hydrocarbon from which it was derived. The 1 atom of H linked by O to the C is peculiar. It is more loosely held than are the others, and easily gives place to other elements or groups.

In the CH_4O of methyl alcohol there are two groups, CH_3 methyl, and HO hydroxyl. Therefore, it may very properly be written CH_3HO, the HO group stamping it as an alcohol. In most respects the alcohols show no basic properties, being neutral in reaction, non-conductors of the electric current, and undissociated into ions. Methyl chlorid lacks some of the properties of a salt. Its aqueous solution is a non-electrolyte, and does not

precipitate silver nitrate. Therefore, there is no amount of dissociated chlorin, such as characterizes metallic chlorids. That there is an exceedingly small percentage of chloridion is shown by the circumstance that the mixture with silver nitrate does, after a long time, throw down a whitish precipitate. This infinitesimal amount of dissociation counts for something and, taken with other facts, justifies the view that alcohols are hydroxyl compounds, but does not warrant the name of salt for the class of which CH_3Cl is a representative. They are known as *esters* (see p. 431).

Ethyl Alcohol (C_2H_6O or C_2H_5HO) (*Spirits of Wine, Grain Alcohol, Ethyl Hydroxid*).—Different varieties of ethyl alcohol are the result of varying degrees of dilution with water. *Absolute alcohol* is free from water, but that officially called absolute has only 99 per cent. of pure alcohol. *Alcohol* (U. S. P.) has a specific gravity of 0.816 and contains 94.9 per cent by volume. This is common alcohol or rectified spirit. *Alcohol dilutum* (U. S. P.) has a specific gravity of 0.930 and contains 48.9 per cent. by volume. It has the concentration of commercial *proof spirit* and is the form used in making some tinctures.

Denatured alcohol, a cheap preparation of grain alcohol for industrial purposes, is free of tax because it contains a small per cent. of methyl alcohol with benzin or pyridin bases, which make it unfit for use in beverages without impairing its value to the arts.

Preparation.—Ethyl alcohol occurs in many beverages which are made from starch and the sweet juices of plants by the action of ferments, and is prepared in three well-defined stages—malting, fermentation, distillation.

Malting.—The starch of corn or of other grain, of rice, or of potatoes is mixed with *malt* and water and kept for several hours at a temperature of about 65° C. (150° F.). In three hours the starch has changed to *dextrin*, *maltose*, and *glucose*. This conversion is brought about by an enzym known as *diastase* or *amylase*, which is generated in grains of barley made into *malt* by the process of sprouting. Diastase is a soluble, unorganized, lifeless principle, like the pepsin of gastric juice. It is a type of the enzyms which hasten chemical action by their presence:

$$\underset{\text{Starch.}}{3(C_6H_{10}O_5)} + H_2O + \text{diastase} = \underset{\text{Maltose.}}{C_{12}H_{22}O_{11}} + \underset{\text{Dextrin.}}{C_6H_{10}O_5}$$

The dextrin later changes to maltose.

$$2(C_6H_{10}O_5) + H_2O = C_{12}H_{22}O_{11}.$$

Fermentation.—The sweet maltose mixture, when cooled, is mixed with *yeast*, a minute plant which grows rapidly, secreting

an enzym, *zymase,* which causes the decomposition of the maltose according to these equations:

$$(1)\quad \underset{\text{Maltose.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose.}}{2(C_6H_{12}O_6)}$$

$$(2)\quad \underset{\text{Glucose.}}{2(C_6H_{12}O_6)} + \text{zymase} = \underset{\text{Alcohol.}}{4C_2H_6O} + 4CO_2.$$

The process is more complex than would appear from this equation, giving the principal end-products. More than one intermediary product and other higher alcohols are formed at the same time in small amount.

Yeast, under the microscope, is seen to be a mass of rounded living cells grouped in clusters. In saccharine solutions containing proteid matter and phosphates these cells, called *saccharomyces,* bud, divide, and send up spore-bearing stems. This plant does not grow freely at temperatures below 5° C. (41° F.) or above 30° C. (86° F.). Kept within these limits, the fluid gives off bubbles of carbon dioxid as if boiling; hence the name *fermentation* (*fervere*=to boil). Above 30° C (86° F.) the alcoholic fermentation declines, but plants different from the yeast cell thrive, causing butyric and other decompositions. These also are called *fermentations,* according to the definition: *fermentation is a transformation of an organic substance, brought about by an enzym produced by living cells.*

Beside zymase, yeast contains the enzym *invertase,* which resolves cane-sugar to glucose, and *maltase* which converts maltose to glucose. (p. 441).

The plant called *mycoderma aceti* secretes an enzym which changes alcohol to vinegar; the plant inducing the lactic-acid fermentation is called the *lactic ferment.*

Another form of fermentation is *putrefaction,* a fetid decomposition of dead nitrogenous organic substances induced by the growth of bacteria. The products of putrefaction are the foul-smelling gases $NH_3 : H_2S : NH_4HS$. Three conditions must be present to bring about any of these fermentations in their proper media: (1) The specific living organism secreting the ferment; (2) a favorable temperature, not below 5° C. (41° F.) nor above 90° C. (194° F.); (3) moisture. To preserve fermentable organic substances unchanged one or more of these three factors must be eliminated: (1) germs, by killing them with antiseptics or by heating to 90° C. (194° F.) (above their death-point) and excluding new spores; (2) warmth, by refrigerators; (3) moisture, by drying out the water, as is done for dried fruit or meat.

Distillation.—The fermented fluid having changed to a weak solution of alcohol is subjected to fractional distillation. The first distillate contains 80 to 90 per cent. of ethyl alcohol and a small amount of the higher alcohols, called *fusel oil.* To get rid

of the fusel oil the raw spirit is filtered through charcoal and again distilled, reserving the middle runnings as *rectified spirit.*

Fermented Beverages.—From malted grains and flavored with hops are made *beer*, *ale*, and *porter*, containing alcohol from 1 to 8 per cent. From the juice of the grape come the *wines* of different alcoholic strength: hock, 8 per cent.; claret, 7 per cent.; sherry, 16 per cent.; port, 20 per cent. From *cider* a hard or fermented liquor is developed of 3 to 7 per cent. alcohol.

Ardent spirits are liquors distilled so as to separate the alcohol and volatile flavoring from the water, non-volatile organic matter, and inorganic salts. *Brandy* (*spts. vini gallici*, U. S. P.) is distilled from wine and has 50 per cent. alcohol. *Whisky* (*spts. frumenti*, U. S. P.) is obtained from fermented grain and has 50 per cent. alcohol. *Gin* (*spts. juniperi*, U. S. P.) is distilled from malted grain flavored with juniper and contains 40 per cent. *Rum* has 45 per cent. and is distilled from fermented molasses. *Liqueurs* or *cordials* are alcoholic spirits made aromatic and sweetened.

Properties.—Pure alcohol is a colorless, volatile liquid of an agreeable odor and burning taste. It quickly absorbs water from the air and mixes with it in all proportions. It boils at 78.5° C. (173.3° F.) and freezes at −130° C. (−202° F.). It burns with a non-luminous flame and without soot. It is a solvent for many substances, gases, resins, essences, and alkaloids. It is a starting-point for making many medicinal and industrial chemicals.

Toxicology.—As a poison, alcohol ranks among the most important because of the prevalence of the habit of alcoholic excess and because of the diseases engendered by long-continued use. The cases of acute alcoholism are especially apt to follow excessive doses of ardent spirits, which may contain fusel oil in addition to the ethyl alcohol.

Physiologic Effects.—In concentrated forms it is a local irritant to the stomach, withdrawing water from the tissues and coagulating albumin. When absorbed in large doses it is a cardiac, respiratory, and cerebral depressant. Doses equal to $\frac{1}{2}$ fl. oz. absolute are almost entirely oxidized in the body in five hours, supplying the place of the carbohydrates of food. Taken in larger amounts, 50 per cent. is eliminated, for the most part unchanged, by the lungs and kidneys.

Symptoms of Acute Alcoholism.—When first seen by the physician, the patient is in profound stupor. He is said to be *dead drunk*, and the odor of alcohol may be detected upon his breath. There is a history of the following symptoms: Confusion of the mind with flushing of the face, nervous excitement and tottering gait, vertigo, foolish speech, muscular weakness, ending in deep stupor. On recovery from the sleep, nausea, headache, and vom-

iting are usually experienced. Though the pupils are usually dilated they are sometimes contracted up to the last moment. It is a good sign when the pupils are sensitive to light. Death from shock may follow in a few minutes after taking a pint of undiluted whisky at one time. When death is not immediate it may occur from coma and syncope or asphyxia.

Fatal Dose.—Taken at one draught, a dose of ardent spirits containing 5 fl. oz. of absolute alcohol may prove fatal. A half-pint of gin has been fatal to an adult. The equivalent of 2 fl. oz. of absolute alcohol would probably be deadly to a child of ten years.

Fatal Period.—Death has occurred in a few minutes; usually it comes on in ten hours, though several days may elapse before the final symptoms.

Treatment.—The first indication is to wash out the stomach through the siphon tube, or to cause vomiting by emetics. Cold and hot affusions may be alternated, and warm applications maintained to the extremities. Strychnin, hypodermically, may be of service to sustain the heart.

Postmortem Appearances.—The odor of alcohol is perceptible in the internal organs. Red, congested, and inflamed areas are seen in the stomach lining. The lungs are usually dropsical. The brain and meninges may be congested and edematous, with venous engorgement and extravasation of blood.

Detection of Ethyl Alcohol.—While the odor is characteristic, this may be due to whisky given as a remedy for the early symptoms of some other condition ending in coma, such as opium-poisoning, uremia, diabetes, cerebral hemorrhage, or concussion of the brain. Being volatile, the alcohol may be separated by acidifying the material with tartaric acid and distilling by passing through it steam from another flask. The distillate is next treated with magnesium oxid and redistilled over the water-bath.

Tests.—*Iodoform Test.*—The alcoholic liquid is mixed with a few drops of solution of iodin in potassium iodid, and then enough potassium hydroxid is added to decolorize it. On gently warming the mixture yellow crystals of iodoform are precipitated. The crystals have the odor of saffron and are hexagonal in form. The same reaction can be obtained from aldehyd, lactic acid, and acetone.

Dichromate Test.—If an aqueous solution of alcohol be added to a mixture of potassium dichromate solution and sulphuric acid, the yellow color turns green from the chromium sulphate formed, and the odor of aldehyd arises, changing to that of acetic acid.

Acetic Ether Test.—Some crystals of sodium acetate are added to the alcoholic solution and the mixture treated with sulphuric acid and warmed; the odor of acetic ether is perceived.

Ethyl Benzoate Test.—A drop of benzoyl chlorid is shaken with the alcoholic liquid and warmed with sodium hydroxid to remove excess of the chlorid. The odor of ethyl benzoate is evolved.

Amyl alcohol, $C_5H_{11}HO$, is the pentacarbon member of the alcohol series. In small amount it is a product of the yeast fermentation in the starch of corn and potatoes. In company with butyl alcohol it is found in an impure mixture known commonly as *fusel oil, oil of grain, oil of potatoes.* As it has a higher boiling-point than ethyl alcohol, it comes over in the last stages of distillation of that spirit. A colorless oily liquid, it has a characteristic unpleasant odor and an acrid taste. It is insoluble in water, floating like an oil. In fusel oil there are two physical isomers of amyl alcohol, one which does not affect the plane of polarized light, and the other which turns it to the right and which boils two degrees higher. By oxidizing agents amyl alcohol is converted to *valeric acid*, which in whisky forms ethyl valerate:

$$C_5H_{11}HO \quad + \quad 2O \quad = \quad H_2O \quad + \quad C_5H_{10}O_2.$$

It is believed that some of the injurious effects of drinking raw whisky and potato spirit are attributable to the presence of this substance with aldehyd. Headache, giddiness, and nausea are among the sequels of intoxication when fusel oil is present. In cases of well-marked poisoning the most prominent symptoms are coma, lasting several hours, followed by glucose in the urine. It has caused dark urine from the presence of methemoglobin.

Whisky kept four years in barrel (U. S. P.) has its fusel oil oxidized to a harmless ester of mellow flavor.

Detection of it as an impurity usually rests upon the characteristic odor emitted by a small quantity when allowed to evaporate from filter paper.

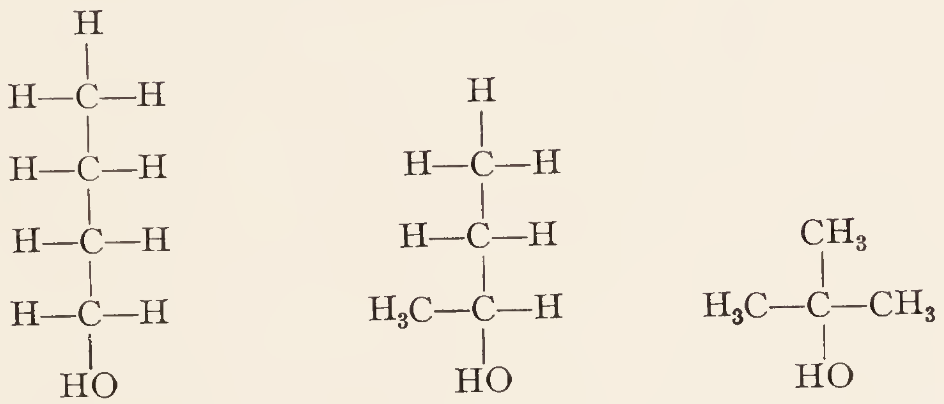
Alcohols in General.—The term alcohol designates a large class of organic compounds which differ in properties and appearance, but are alike in being hydroxyl derivatives of saturated hydrocarbons. As the radicals differ in their valence they are named according to the number of hydroxyl groups they take; monohydric or monatomic; dihydric or diatomic; trihydric or triatomic. The monohydric alcohols, parallel with the methane series and homologous with common alcohol, and having medical importance, are:

			B.-P.	Sp. Gr. at 0°.
Methyl alcohol	CH_3HO	66° C.	(150.8° F.)	0.796.
Ethyl "	C_2H_5HO	78° C.	(172.4° F.)	0.806.
Propyl "	C_3H_7HO	97° C.	(206.6° F.)	0.817.
Butyl "	C_4H_9HO	117° C.	(242.6° F.)	0.823.
Amyl "	$C_5H_{11}HO$	132° C.	(289.6° F.)	0.825.

Three alcohols can be prepared from propane, C_3H_8: monatomic propyl alcohol, C_3H_7HO; diatomic propylene alcohol, $C_3H_6(HO)_2$; and triatomic propenyl alcohol, $C_3H_5(HO)_3$. The diatomic alcohols are called *glycols* after ethylene glycol (p. 402).

There may be alcohols with even more hydroxyl groups, tetratomic, pentatomic, etc. Mannitol is a hexatomic alcohol with six carbon atoms, each having a hydroxyl group attached.

Another division is made of alcohols into *primary*, *secondary*, and *tertiary*, according as the facts warrant graphic formulas which show that the carbon atom combined with hydroxyl is at the same time directly united with 1, 2, or 3 other carbon atoms. Thus, there are three butyl alcohols having the formula C_4H_9HO. There is good reason for employing the following graphic formulas to express their differences in structure:



Primary butyl alcohol. Secondary butyl alcohol. Tertiary butyl alcohol.

$(C_3H_7 . CH_2OH)$ $(C_2H_5 . CH_3 . CHOH)$ $(CH_3 . CH_3 . CH_3 . COH.)$

A *primary* alcohol is one in which the carbon atom in union with the hydroxyl is directly united with only 1 other carbon atom; a *secondary* alcohol is one in which the carbon atom in union with the hydroxyl is directly united with 2 other carbon atoms; a *tertiary* alcohol is one in which the carbon atom in union with the hydroxyl is directly united with 3 other carbon atoms. There is a decided difference among these three alcohols, especially in their behavior under the action of oxidizing agents. Thus:

Primary alcohols are converted first into aldehyds, next into acids containing the same number of carbon atoms, and on further oxidation break up (pp. 407 and 418).

Secondary alcohols are converted into acetones, which upon further oxidation break up into acids with a smaller number of carbon atoms (p. 413).

Tertiary alcohols are decomposed without previous formation of aldehyds or acetones, yielding acids with a smaller number of carbon atoms.

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DIHYDRIC ALCOHOLS OR GLYCOLS

The members of this group are called *glycols*, after the name of the simplest one, $C_2H_4(OH)_2$, *ethylene glycol*, which corresponds with ethyl alcohol.

Ethylene Glycol.—When ethylene bromid, $C_2H_4Br_2$, is heated with a dilute alkali the bromin is replaced by hydroxyl, and ethylene alcohol is obtained. Its structure is indicated by this equation:

$$\begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix} + 2KOH = \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} + 2KBr.$$

Properties.—Ethylene glycol is a thick colorless liquid with a sweetish taste, freely soluble in water and alcohol. It is a type of the class, all being neutral oily liquids, prepared by boiling the dibromo-additive products of the olefins with alkalis. In composition they have two hydroxyl groups, thus differing from monohydric alcohols as calcium hydroxid, $Ca(OH)_2$, differs from potassium hydroxid, KOH. With monobasic acids they form two esters, neutral and alcoholic. Thus, mono-acetic glycol has one alcoholic group left in it, $CH_2(C_2H_3O_2).CH_2OH$, while diacetic glycol has all the hydroxyl replaced by the acid, $CH_2(C_2H_3O_2).CH_2(C_2H_3O_2)$.

Under the action of oxidizing agents one alcoholic group changes to COOH, characteristic of acids, and an oxyacid is formed. If both alcoholic groups are oxidized a diacid is the product. Thus:

Glycol.	Oxyacetic acid.	Oxalic acid.
$\begin{matrix} CH_2OH \\ \vert \\ CH_2OH \end{matrix}$	$\begin{matrix} COOH \\ \vert \\ CH_2OH \end{matrix}$	$\begin{matrix} COOH \\ \vert \\ COOH \end{matrix}$

TRIHYDRIC ALCOHOLS

On a preceding page it has been stated that the paraffin propane, by substitution of hydroxyl groups successively, can be converted, first, into monohydric propyl alcohol, C_3H_7OH; next, into dihydric propylene alcohol, $C_3H_6(OH)_2$; and, last, to *trihydric propenyl alcohol*, $C_3H_5(OH)_3$. This last named is the only trihydric alcohol prepared with ease and which has been well studied. It is used in medicine under the common name of *glycerin*. The three groups containing hydroxyl are represented in the formula: $CH_2OH, CHOH, CH_2OH$. The trihydric class corresponds to the metallic bases, like bismuth hydroxid, $Bi(OH)_3$.

Glycerinum, U. S. P., **Glycerol** ($C_3H_5(OH)_3$) (*Glycerin, Propenyl Alcohol*, or *Glyceryl Alcohol*).—This is obtained by the action of superheated steam, by fermentation, or by saponification upon

fats which are not very stable compounds of weak fatty acids with glycerol, which is weakly basic.

$$\underset{\text{Tristearin.}}{C_3H_5(O.C_{18}H_{35}O)_3} + 3H_2O = \underset{\text{Glycerin.}}{C_3H_5(OH)_3} + \underset{\text{Stearic acid.}}{3(C_{18}H_{35}O.OH)}$$

After separation of the pasty mass of stearic acid the aqueous distillate is decolorized by charcoal and concentrated by evaporation. Redistillation is used to free it from the water which is collected in the first fractions condensed.

Properties.—When anhydrous, glycerin is a colorless crystal, but as commonly prepared contains some water, and is then an odorless thick liquid with a specific gravity of 1.246 at 25° C. (77° F.). It is very hygroscopic, absorbing water from the air, and is freely miscible with water and alcohol, but not with ether and chloroform. It is a solvent for many solids and liquids, the official solutions, called *glycerites*, are concentrated, permanent, and water-soluble. The taste is sweet, a property common to the glycols and other alcohols containing many hydroxyl groups, such as mannitol and dulcitol. Glycerin is an antiputrescent and antiseptic, but undergoes decomposition into acrolein and water under the action of heat and various chemicals.

Tests.—*Acrolein Test.*—Heated with sulphuric acid it splits off 2 molecules of water, leaving *acrolein*, a colorless liquid, giving an irritating vapor with an unpleasant odor like burning grease:

$$\underset{\text{Glycerol.}}{C_3H_5(OH)_3} = \underset{\text{Acrolein.}}{C_3H_4O} + 2H_2O.$$

Fehling's Test.—Adulterations with glucose are detected by Fehling's test (see p. 618). Pure glycerin does not respond to this test nor will it ferment with yeast.

Borax Test.—Having fused borax in a platinum loop the bead is wet with glycerin and again heated. A green color to the flame shows that boric acid has formed a volatile ester with the glycerin.

ETHERS (Simple and Mixed)

In another place reasons were given for regarding alcohols as hydroxids of hydrocarbon radicals. If hydroxyl be considered as derived from water by the loss of 1 atom of hydrogen, then alcohols, as hydroxids, may be constructed on the water plan by replacing that atom of hydrogen with the radical. Thus, water being $\begin{matrix}H\\H\end{matrix}\!>O$, ethyl alcohol is $\begin{matrix}C_2H_5\\H\end{matrix}\!>O$.

By substituting another ethyl group for the remaining atom of hydrogen in hydroxyl, we get an oxid. Thus, $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>O$ (p. 373).

This oxid, $(C_2H_5)_2O$, is a substance long known as *ether*. Other monovalent radicals can be linked by oxygen in the same way, and thus give rise to a class of oxids or *ethers* named after the radicals contained in them. In the series of *simple ethers*, $(CH_3)_2O$, is methyl ether; $(C_2H_5)_2O$ is ethyl ether, the official form. By manipulation at the right moment the 2 hydrogen atoms may be replaced by two different radicals, making a *mixed ether*, such as $\begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!\!>\!O$, *methylethyl ether.*

The ethers bear the same relationship to the metallic oxids that the alcohols do to the metallic hydroxids:

$C_2H_5 . OH$	corresponds to	$K . OH$.
$C_2H_5 . O . C_2H_5$	"	$K . O . K$.

As ether contains no HO group it is unaffected by potassium and does not form esters with weak acids like those made by alcohol.

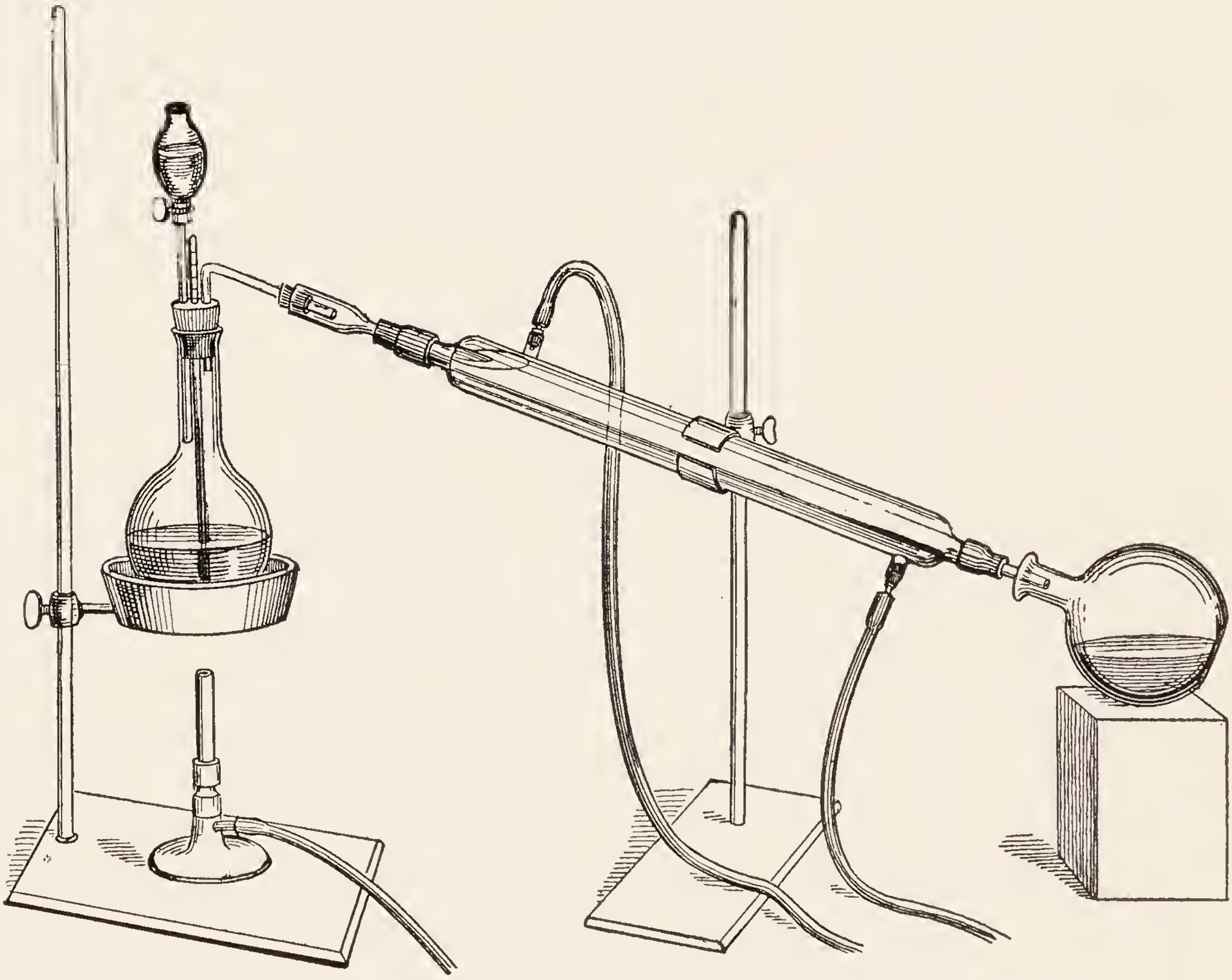


FIG. 77.—Apparatus for making and distilling ether.

Ethyl ether ($C_4H_{10}O$) (*æther, sulphuric ether, ethyl oxid*) is prepared by a *continuous process* of distilling alcohol with concentrated sulphuric acid. A flask having a thermometer and a delivery tube connected with a condenser (Fig. 77) is fitted with

a funnel having a stop-cock. The funnel is charged with 90-per cent. alcohol and the tap closed. Five parts of alcohol and 9 parts of sulphuric acid are heated in the flask to the boiling-point, 140° C. (284° F.). This temperature is maintained, for it is the point at which ether distils over, and at which alcohol remains in the flask. From the funnel fresh alcohol is slowly supplied to take the place of the ether which collects in the receiver. In the flask there accumulates water to dilute the sulphuric acid, which ultimately becomes too weak to act. Up to that limit the same small quantity of acid serves to convert a large quantity of alcohol to ether. On comparing the molecular formula of ether, $C_4H_{10}O$, with a proportional formula (2 molecules) of alcohol, $2C_2H_6O$ or $C_4H_{12}O_2$, it is seen that

$$C_4H_{10}O \quad = \quad C_4H_{12}O_2 \text{ minus } H_2O;$$

that is, ether is the anhydrid of alcohol, the elements of water being abstracted by sulphuric acid. The process has two stages, as shown in the equations:

$$\underset{\text{Alcohol.}}{\begin{matrix}C_2H_5\\H\end{matrix}\!>\!O} \quad + \quad \underset{\text{Sulphuric acid.}}{\begin{matrix}H\\H\end{matrix}\!>\!SO_4} \quad = \quad \underset{\text{Ethyl hydrogen sulphate.}}{\begin{matrix}C_2H_5\\H\end{matrix}\!>\!SO_4} \quad + \quad H_2O.$$

$$\begin{matrix}C_2H_5\\H\end{matrix}\!>\!SO_4 \quad + \quad \begin{matrix}C_2H_5\\H\end{matrix}\!>\!O \quad = \quad \begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!O \quad + \quad H_2SO_4.$$

If a mixture of two alcohols be used, the distilled product will consist of three ethers. Thus, methyl and ethyl alcohols yield methyl ether, ethyl ether, and the mixed methylethyl ether, $CH_3 . O . C_2H_5$.

Properties.—Ether is a colorless, neutral, mobile liquid with a characteristic sweetish smell. Its specific gravity is 0.716; its boiling-point 35° C. (95° F.). The official ether (æther, U. S. P.) contains 4 per cent. of alcohol, which raises the boiling-point. Ether is highly volatile and inflammable. Exposed to the air, an explosive mixture of its vapor and air at once forms, which renders experimentation with it dangerous and its administration near an open flame unsafe. When this exposure is unavoidable, the light should be well above the ether, as its vapor, being heavier than the air, settles down.

$$\underset{\text{Ether.}}{C_4H_{10}O} \quad + \quad \underset{\text{Air.}}{6O_2} \quad = \quad 4CO_2 \quad + \quad 5H_2O.$$

Experiment.—Into a slightly warmed beaker put 2 c.c. of ether and cover it until the ether has filled the beaker with vapor.

Pour the heavy vapor into an empty beaker and prove its presence by a lighted taper.

Miscible in all proportions with alcohol, chloroform, and other organic liquids, ether requires 10 volumes of water to dissolve it. In the arts it is used as a solvent for oils, resins, alkaloids, bromin, and iodin. In surgery it is used enormously as an anesthetic, the physiologic effects being those of alcohol, but the narcotism comes on more promptly and is more transient. When sprayed on the skin its rapid evaporation lowers the temperature and causes a local numbness. *Spiritus ætheris*, U. S. P., contains 1 part of ether with a little more than 2 parts of alcohol. Dose: 1 fl. dr. (4 c.c.). *Spiritus ætheris compositus* (*Hoffman's anodyne*) is a mixture of 1 part of ether and 2 parts of alcohol with 2.5 per cent. of ethereal oil. Dose: 5 to 60 ♏ (0.33–4 c.c.).

Toxicology.—As an anesthetic, ether is safer than chloroform, the record justifying expectation of 1 death in 12,000 etherizations. It is sometimes used for suicidal purposes and as a habitual intoxicant. Kept unsealed or in glass it generates acetaldehyd.

Symptoms.—When inhaled, the vapors irritate the larynx and increase the flow of saliva and mucus. Unconsciousness comes on soon, the pulse and breathing becoming slow and irregular. An overdose may cause death by asphyxia. Notably dangerous is the *sequel*, in the shape of pneumonia from pulmonary irritation. When taken by the stomach, ether causes a sense of local irritation in stomach and bowels, and symptoms of general intoxication come on quickly.

Fatal Dose.—By inhalation death has followed 2½ fl. oz. (75 c.c.). Continuous inhalation of air containing 6 per cent. of ether vapor arrested respiration in ten minutes. Anesthesia may be induced with about half that concentration in the same period of time.

Fatal Period.—Failure of respiration may occur before or after full unconsciousness. The pulmonary and renal sequels may cause death days after recovery from the narcotism.

Treatment.—The immediate indication is for fresh air and respiratory stimulants, such as ammonia, artificial respiration, oxygen mixed with carbon dioxid, and hypodermic doses of strychnin.

Detection.—If not identified by odor or information from the surroundings, the detection is most difficult, as the ether quickly escapes from the body by its vaporization. A few drops may be recovered by distillation at a low heat and condensation in receivers surrounded by a mixture of salt and ice. The distillate will have the ethereal odor, will burn quickly, evaporate, and its vapor will turn to green the yellow spot made on filter paper with potassium bichromate and sulphuric acid.

ALDEHYDS

These compounds are the first stage in the process of oxidation of alcohols, the next products being the acids. As the first effect of oxidizing an alcohol is the abstraction of 2 atoms of hydrogen to form water, the resulting compound is named by blending significant syllables from the phrase "*al*cohol *dehyd*rogenatum."

$$\underset{\text{Methyl alcohol.}}{CH_4O} \quad + \quad O \quad = \quad \underset{\text{Formaldehyd.}}{CH_2O} \quad + \quad H_2O.$$

$$\underset{\text{Ethyl alcohol.}}{C_2H_6O} \quad + \quad O \quad = \quad \underset{\text{Acetaldehyd.}}{C_2H_4O} \quad + \quad H_2O.$$

The structural changes are represented by graphic equations thus:

$$\text{(i)}\quad \underset{\text{Methyl alcohol.}}{\begin{array}{c} H \\ | \\ H-C-O-H \\ | \\ H \end{array}} \quad + \quad O \quad = \quad \underset{\text{Formaldehyd.}}{\begin{array}{c} H \\ | \\ H-C=O \end{array}} \quad + \quad H_2O.$$

$$\text{(ii)}\quad \underset{\text{Formaldehyd.}}{\begin{array}{c} H \\ | \\ H-C=O \end{array}} \quad + \quad O \quad = \quad \underset{\text{Formic acid.}}{\begin{array}{c} O.H \\ | \\ H-C=O. \end{array}}$$

Structure.—With phosphorus pentachlorid the aldehyds yield phosphoric oxychlorid and ethyledene chlorid, thus:

$$\underset{\text{Ethyl aldehyd.}}{C_2H_4O} \quad + \quad PCl_5 \quad = \quad POCl_3 \quad + \quad C_2H_4Cl_2.$$

The atom of oxygen alone is replaced by 2 of chlorin, which would not happen if the oxygen were in a hydroxyl group, but is possible if the oxygen be in carbonyl, CO, where it is in combination with carbon by both affinities, $C=O$. The simplest aldehyd is formic aldehyd, CH_2O, and there is but one way of expressing its constitution graphically: $H-C\Big\langle{}^{H}_{O}$. The peculiar properties of aldehyds are due to the group $-C\Big\langle{}^{H}_{O}$. Acetic aldehyd then becomes $CH_3-C\Big\langle{}^{H}_{O}$. Under certain conditions formaldehyd forms additive compounds as if it were not wholly saturated: its valence at such times is expressed by the graphic formula $\begin{array}{c} H-C\Big\langle{}^{H}_{O-} \\ | \end{array}$.

Formaldehyd, H . COH or CH_2O, can be formed by oxidizing methyl alcohol vapor, through the catalytic agency of incandescent platinum. This reaction is much accelerated when the platinum is finely divided, as spongy platinum. When calcium formate is heated formaldehyd comes off as a vapor:

$$Ca(H.CO_2)_2 = CaCO_3 + H.CHO.$$

It is a colorless gas with a strong pungent odor, and condenses at −21° C. (−5.8° F.) to a colorless liquid. It is readily soluble in water, making a colorless volatile liquid which is a convenient preparation for medicinal use. The 40-per cent. aqueous solution is called *liquor formaldehydi*, U. S. P., and sometimes *formalin*. By heat it evolves the gas with some steam. It is of great value in hardening and preserving anatomic specimens and as a germicide, antiseptic, and deodorizer. The aldehyds are unstable, and not being saturated compounds they readily join to other elements or groups. Intermediate between alcohols and acids, they take oxygen to form the latter or take hydrogen to make the former. Thus:

$$CH_2O + O = CH_2O_2 \text{ (Formic acid).}$$
$$CH_2O + H_2 = CH_4O \text{ (Methyl alcohol).}$$
$$CH_2O + NH_3 = CH_3ONH_2 \text{ (Aldehyd ammonia).}$$
$$CH_2O + H_2S = H_2O + CH_2S \text{ (Sulphaldehyd).}$$

Like other lower aldehyds it forms an additive compound with sodium bisulphite which is soluble. (See Hexamethylenamin p. 504.)

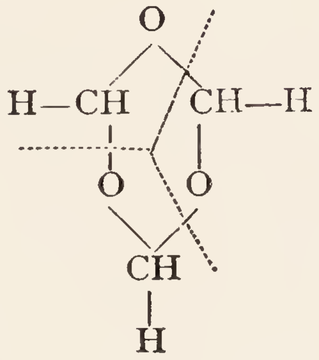
For disinfecting a closed room the *liquor formaldehydi* may be vaporized by heat or sprayed. The vapor combines directly with the albumin of the bacterial cell and destroys its reproductive powers. An approved method known as *permanganate formalin* depends upon the fact that potassium permanganate oxidizes a portion of the formaldehyd to formic acid, liberating enough heat to evaporate the remainder. A deep tin pail is warmed and then receives the permanganate as crystals or powder, 8½ oz. for every 1000 cu. ft. of room space. Upon this 20 fl. oz. of formalin is poured. Effervescence begins at once, the room is closed, and the operation is over in five or ten minutes without the use of a lamp. After twelve hours the room is opened and the odor removed by sprinkling ammonia. Clothing and furniture are uninjured.

Paraformaldehyd [$(CH_2O)_n$] (*Tri-oxymethylene*).—In the anhydrous state, in concentrated solution, or even in the hydrated official solution when moderately heated, formaldehyd *polymerizes* readily. Two or more molecules join to form one of the solid modifications shown in the reversible equations:

$$2CH_2O \rightleftarrows (CH_2O)_2, \text{ Paraformaldehyd.}$$
$$3CH_2O \rightleftarrows (CH_2O)_3, \text{ Trioxymethylene.}$$

The first is a colorless, amorphous solid, melting at 171° C. (339° F.), subliming at a slightly higher temperature, and when strongly heated breaking up into gaseous formaldehyd. As the gas cools paraformaldehyd is again obtained. The formation of the gas may be shown by Schiff's reaction, using paper wet with decolorized fuchsin. (See Tests.)

Polymerism is the condition of a substance where the molecules in their original proportion are joined into a more complex group, like the change in nitrogen peroxid—$2NO_2 \rightleftarrows N_2O_4$. The different modifications are similar to the allotropic forms of elements, and their relationship to one another resembles that of yellow and red phosphorus. The constitution of the *polymer* of formaldehyd, $(CH_2O)_3$, is usually represented by the graphic formula below, the dotted lines showing the method of union:



Toxicology of Formaldehyd.—In spite of its reputation as a disinfectant harmless to man, there are many instances of inflammation of the conjunctiva and air-passages among those who manufacture formaldehyd, or who breathe its vapor when disinfecting houses. The higher animals are injured, if not killed, by the vapor when it is present in sufficient strength to destroy infectious germs. Under the names *preservalene* and *freezene* it is widely used by dairymen to preserve milk in hot weather. In any but the smallest amounts it inhibits the action of the digestive ferments and causes indigestion and imperfect assimilation. Very small amounts suffice to preserve milk for several days with very little retarding effect on digestion, but the mixture should be labeled *preserved.* (See Milk, p. 582.)

Symptoms.—Solutions containing 1 part in 2000 irritate the skin, causing eczema, ulcerations, and even gangrene. When the 40 per cent. liquid is taken in doses of ½ oz. or more, the symptoms are pain in the mouth and abdomen, vomiting, giddiness, diarrhea with straining, urinary suppression, and recovery or, may be, death by dyspnea and syncope.

Treatment.—After evacuating the stomach dilute spirits of ammonia will be of help. The odor of its vapor in a room is at once removed by ammonia vapor.

Test.—For detection of the presence of formaldehyd in milk see p. 583. When in a solid form, the material, minced, is digested for an hour at 80° C. (176° F.) in water acidified with sulphuric

acid. Dry powdered sodium sulphate in excess is added, and the paste distilled. If the first portions of the distillate contain formaldehyd, it will respond to the following tests:

Schiff's Fuchsin Reaction.—Dissolve 0.2 gm. of rosanilin or the hydrochlorid in 10 c.c. of a freshly prepared, *saturated* aqueous solution of sulphur dioxid. Allow the solution to stand until all signs of pink disappear and it becomes colorless or pale yellow. Then dilute with water to 200 c.c. and preserve for use in a tightly stoppered bottle. It turns pink or violet with formaldehyd.

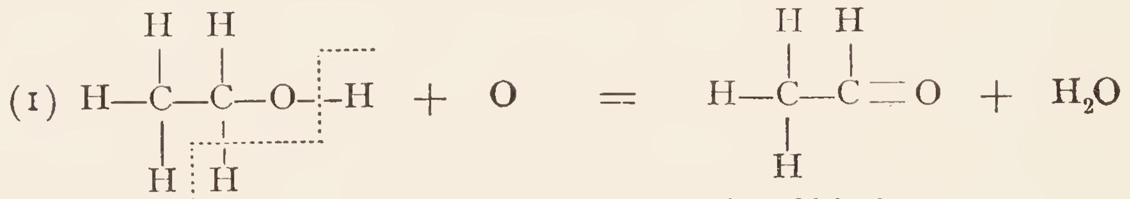
With light excluded, the reagent keeps well. If necessary its sensitiveness may be restored by addition of sodium acetate till a pink color appears, which is discharged by a few drops of the original reagent. Not only do aldehyds redden it, but also alkaline solutions, heat, or prolonged exposure to the air.

When the formaldehyd is in a gaseous state, the test may be applied by hanging in the air filter-paper wet with the reagent.

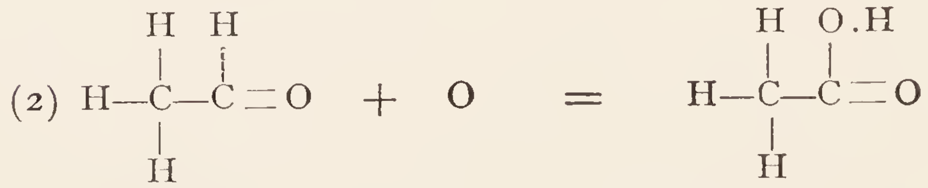
Resorcin Test.—Having made a solution of 5 parts of resorcin in 100 of potassium hydroxid (40 per cent.), a portion is heated with an equal volume of formaldehyd, and a red color is obtained. (For *Hehner's* Test in Milk, see p. 583; *Rimini's* Test in Urine or Milk, p. 650.)

Acetaldehyd ($CH_3.CHO$) (*Acetic Aldehyd*).—This is formed by the oxidation of ethyl alcohol in the operation of distilling a mixture of alcohol, manganese dioxid, and sulphuric acid. The distillate is a mixture which is redistilled below 50° C. (122° F.). The second distillate is mixed with ether and saturated with ammonia to get a crystalline precipitate of *aldehyd ammonia.* This substance, distilled with dilute sulphuric acid at a low temperature, yields a dilute aldehyd. The water is removed with calcium chlorid. Acetic aldehyd is a colorless, volatile, inflammable liquid, boiling at 20.8° C. (69° F.). Its odor is suffocating, like that of sulphur dioxid. It is soluble in water, alcohol, and ether, and acts as a reducing agent on ammoniacal solutions of silver.

The formation of aldehyd from ethyl alcohol by abstracting H_2 is shown in equation (1); in equation (2) is shown how acetic acid is formed by oxidation of the aldehyd:



Ethyl alcohol. Acetaldehyd.



Acetaldehyd. Acetic acid.

Acetic aldehyd is a rapid intoxicant, inducing profound stupor and deleterious after-effects, such as attend the drinking of *high wines*—raw spirits which have not been deprived of it, as they should, before being taken internally.

Three polymerids of aldehyd are known: *aldol*, $(C_2H_4O)_2$; *paraldehyd*, $(C_2H_4O)_3$; and *metaldehyd*, $(C_2H_4O)_n$.

Paraldehyd is formed when a drop of sulphuric acid is added to aldehyd. There is violent action and a change to a more pleasant-smelling liquid with a burning taste, boiling at 124° C. (255° F.) and solidifying by cold. It is soluble in water, and if distilled with dilute sulphuric acid goes back to aldehyd.

Toxicology.—Its physiologic effects in doses of 30 to 60 min. (2–4 c.c.) are those of a soporific like chloral, but with less depression of the heart. It gives a strong disagreeable odor to the breath and the urine. A very large amount, such as 3 fl. oz. (90 c.c.), will cause nausea, vomiting, vertigo, headache, ending in profound stupor. Habitual use of it in doses of 2 oz. (60 c.c.) leads to a deplorable condition, characterized by mental weakness, dyspepsia, sleeplessness, and delusions.

Treatment.—The indications are the same as in poisoning from chloral.

Detection.—Paraldehyd does not give the reactions nor show the ordinary properties of aldehyd. It must first be converted to aldehyd by distilling with steam, the suspected material having been first acidified by sulphuric acid. The distillate should give Schiff's reaction with fuchsin (see Formaldehyd, p. 408).

Tollen's Test.—A deposit occurs of a silver mirror on the glass of a test-tube that has been cleaned with hot caustic soda and washed with distilled water, when weak aldehyd is added to ammoniacal solution of silver oxid:

$$CH_3 . CHO + Ag_2O = CH_3CO . OH + 2Ag.$$

This is a very sensitive test. The reagent is made by dissolving 3 gm. of silver nitrate in 30 gm. of 25 per cent. ammonia water and adding 3 gm. of sodium hydroxid dissolved in 3 c.c. of water.

Chloral ($CCl_3 . COH$) (*Trichloraldehyd*).—This most important derivative of acetic aldehyd is prepared by saturating absolute alcohol with dry chlorin. The first product is a crystalline substance which is shaken with sulphuric acid and distilled. The distillate treated with lime and again distilled yields chloral. The syllable *-al* used as a suffix indicates an aldehyd. Thus acetic aldehyd is sometimes called *ethanal*, to indicate that it is the aldehyd formed from *ethanol* (ethyl alcohol). *Chloral* is an abbreviation for *chlorethanal*. The first effect of chlorin is to convert the

alcohol to aldehyd by extracting two hydrogen atoms to make 2HCl; the second is to chlorinate the aldehyd:

$$\underset{\text{Aldehyd.}}{CH_3CHO} + 3Cl_2 = \underset{\text{Choral.}}{CCl_3CHO} + 3HCl.$$

Chloral is a colorless oily liquid with a pungent odor and acrid taste. Its reactions show it to be an aldehyd in its chemical properties. It is soluble in water, and in a small amount of the solvent it forms a colorless crystalline compound, *chloral hydrate*, $CCl_3COH \cdot H_2O$.

On heating with an alkali, chloral yields chloroform and a formate:

$$\underset{\text{Chloral.}}{CCl_3CHO} + KOH = \underset{\text{Chloroform.}}{CHCl_3} + \underset{\text{Potassium formate.}}{H \cdot COOK}$$

Chloralum hydratum (U. S. P.) occurs as volatile crystals having a odor like that of a melon and a taste the unpleasant nature of which is masked by solution in beer, whisky, or wine. It is soluble in water, alcohol, and ether. Dose: 10 to 25 gr. (0.66–1.62 gm.). It is *incompatible* chemically with alcohol, potassium iodid, carbolic acid, and camphor.

Toxicology.—*Acute poisoning* occurs from accidental overdosing, also from criminally mixing it with the drink of a victim, when it is known as *knock-out drops*. At no stage does it exhilarate like alcohol, nor does it relieve pain like chloroform until a full hypnotic dose has caused sleep. With massive doses the soporific effects are much like those of heavy doses of alcohol or chloroform. The skin is cold and clammy; the brain and spinal centers are depressed and finally paralyzed. As a gastric irritant it may first cause nausea and vomiting, but deep coma soon sets in with thready pulse and feeble respiration, growing more shallow and irregular until it ceases altogether. *Chronic poisoning* is quite common, the habit of *chloral tippling* being formed to cure insomnia. In time varied symptoms are produced, such as indigestion, wasting, skin eruptions, conjunctivitis, pains, wakefulness, nervous depression with melancholia, and death from heart failure.

Dose.—The maximum safe dose is 20 gr. (1.29 gm.), repeated twice at intervals of an hour.

Postmortem Appearances.—Characteristic changes are not found at the autopsy.

Treatment.—The stomach should be promptly evacuated and washed out with warm alkaline water. If no tube be at hand, then apomorphin, in hypodermic doses of 5 min. of a 2 per cent. solution, or other emetics, may be used. To rouse the heart

strong coffee may be given by mouth or rectum, and hypodermic injections of 2 or 3 min. of a 2 per cent. solution of strychnin nitrate. Applications of hot bottles and blankets, flicking the face with a wet towel, artificial respiration, and oxygen, are measures that may prove of service to combat the depression.

Fatal Dose.—Three grains have proved fatal to a child one year old. Ten grains have proved fatal to a woman of seventy with a weak heart. On the other hand, recovery has followed doses of more than half an ounce.

Tests.—In the urine some chloral is eliminated unchanged, but most of it forms a compound with glycuronic acid called urochloralic acid, which may be mistaken for glucose, as it reduces the copper sulphate of Fehling's solution. As urochloralic acid and its salts are levorotatory to polarized light, by means of the polariscope we can distinguish between "chloral urine" and "sugar urine," which is dextrorotatory. If the urine be acidified with sulphuric acid and shaken with ether in a separating funnel, the ether takes up the chloral and on evaporation leaves it as a solid residue. The contents of the stomach should be digested for twenty-four hours with four volumes of absolute alcohol acidified with sulphuric acid; then filtered and evaporated. Petroleum ether will remove fat and sulphuric ether will extract the chloral.

Tests may be applied to the ethereal residue. Strong alkalis warmed convert chloral to chloroform, yielding the familiar odor of that substance. The chloroform may be identified by the Ragsky process, the *betanaphthol* test, and the offensive *isobenzonitril test* (pp. 389, 390).

Chloral, having in it the group CHO, like other aldehyds, reduces Fehling's solution (p. 618).

To determine the quantity of chloral dissolved magnesia is first used to neutralize acids, and a measured amount of normal solution of sodium hydroxid is added to render the solution distinctly alkaline. The excess is estimated by a normal oxalic-acid solution, and, subtracted from the original amount, gives the proportion taken up by the chloral. For 1 c.c. of normal sodium hydroxid that has united with the chloral calculate 0.1655 gm. of chloral.

KETONES (Acetones)

The interesting substance called *acetone*, or *dimethyl ketone*, $CH_3 . CO . CH_3$, belongs to a class of compounds produced by the incomplete oxidation of secondary alcohols (p. 401). If secondary propyl alcohol be oxidized, 2 atoms of hydrogen are abstracted, just as when a primary alcohol is so treated. But the

primary alcohol forms an aldehyd, while the secondary alcohol forms a ketone. Thus:

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CHOH \quad + \quad O \quad = \quad \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO \quad + \quad H_2O.$$

Secondary propyl alcohol. Acetone.

All ketones are regarded as containing divalent carbonyl, $=CO$, linking together 2 hydrocarbon radicals. A *mixed* ketone is one which contains 2 different radicals, as methylethyl ketone, $CH_3 . CO . C_2H_5$. Both ketones and aldehyds may be regarded as derived from the paraffins by substituting 1 atom of oxygen for 2 atoms of hydrogen; they are, therefore, isomeric. Thus, C_3H_6O is the empiric formula for acetone, $CH_3 . CO . CH_3$, and also for propaldehyd, $CH_3 . CH_2 . CHO$. The difference of constitution is shown by the further action of oxygen, which causes a ketone to break up into a mixture of two or more acids, but unites with an aldehyd to make a single corresponding fatty acid. They have, however, many resemblances in chemical behavior, such as the similar reaction with phosphorus pentachlorid, explicable from the fact that both contain the carbonyl group (p. 407):

$$\text{Acetone, } \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O. \quad \text{Aldehyd, } \begin{matrix}H\\CH_3\end{matrix}\!\!>C=O.$$

Ketones are more stable than aldehyds, as they have no available hydrogen left for oxidation; they do not reduce alkaline solutions of copper and other metallic salts, nor do they combine directly with alcohols or with ammonia. They do not polymerize, as do the aldehyds. Their names always have the suffix *-one*.

Acetone is the most important ketone. It can be prepared by the dry distillation of sugar, tartaric acid, or the acetates:

$$Ca(CH_3CO_2)_2 \quad = \quad (CH_3)_2CO \quad + \quad CaCO_3.$$

Calcium acetate. Acetone.

It is a mobile, colorless liquid, with a pleasant ethereal odor, specific gravity 0.792. It boils at 56° C. (132.8° F.), is miscible with water, alcohol, and ether. It dissolves fats, resins, and guncotton. In diabetes and some other diseased states it exists in the blood and urine, and its peculiar odor may be detected on the breath. With its congeners, diacetic acid and oxybutyric acid, it is probably due to faulty fat-metabolism and contributes to bring on the symptoms of diabetic coma.

Tests for Acetonuria.—(1) Distil 25 c.c. from 500 c.c. of urine, which has been acidulated with phosphoric acid to prevent frothing,

and apply the iodoform test by adding a small quantity of iodin and dropping in potassium hydroxid until the iodin color disappears. The odor of iodoform is recognized, and soon a yellow crystalline precipitate appears.

(2) Without distilling, add to the urine an excess of a solution of 5 gm. of fresh mercuric oxid in 100 c.c. of 2 per cent. sulphuric acid. By filtration remove the precipitate and boil the filtrate for several minutes. A white precipitate or even a cloudy appearance denotes acetone.

SULPHUR DERIVATIVES OF THE PARAFFINS

Not only does sulphur form a series of mineral compounds parallel with those of oxygen, but also a class corresponding to the simple ethers, alcohols, aldehyds, acids, and ketones, which are oxygen derivatives of the paraffins. These are named from *theion* (sulphur) as *thio*-alcohols, *thio*-ethers, *thio*-aldehyds, *thio*-acids, *thio*-ketones. In addition, sulphur forms compounds which have no oxygen counterpart, such as the sulphoxids, sulphones, and sulphonic acids. Two classes of compounds are formed by the action of hydrogen sulphid upon the alcohols—namely, hydrosulphids and sulphids. The relationship of these to alcohols and ethers is shown by the formulas:

Ethyl alcohol or hydroxid.............................. $C_2H_5 . OH$.
Ethyl thio-alcohol or hydrosulphid.............................. $C_2H_5 . SH$.
Ethyl ether or oxid.............................. $(C_2H_5)_2O$.
Ethyl thio-ether or sulphid.............................. $(C_2H_5)_2S$.

The thio-alcohols or organic hydrosulphids have been long known as *mercaptans* (*mercurium captans*) because they readily seize on mercuric oxid to form crystalline compounds, called *mercaptids* or *thio-ethylates:*

$$\underset{\text{Ethyl mercaptan.}}{2C_2H_5 . SH} + HgO = \underset{\text{Mercuric mercaptid.}}{(C_2H_5 . S)_2Hg} + H_2O.$$

Ethyl Mercaptan ($C_2H_5 . SH$) (*Thio-alcohol*).—This substance has become important as the material from which the drug *sulphonal* is made. It is prepared by the action of ethyl chlorid on potassium hydrosulphid:

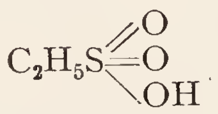
$$C_2H_5Cl + KHS = C_2H_5 . SH + KCl.$$

It is a colorless neutral liquid, with an unpleasant odor, like that of garlic. It boils at 36.2° C. (97.2° F.). Other mercaptans are obtained by similar reactions. They all have disagreeable odors, and in chemical properties resemble ethyl mercaptan.

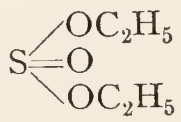
Thio-ethers or **sulphids,** like *ethyl sulphid* $(C_2H_5)_2S$, are made by distilling salts of ethyl sulphuric acid with potassium sulphid:

$$\underset{\text{Ethyl potassium sulphate.}}{2C_2H_5 . KSO_4} + K_2S = \underset{\text{Ethyl sulphid.}}{(C_2H_5)_2S} + 2K_2SO_4.$$

Sulphonic acids are acids containing the group $SO_2 . OH$ attached to a hydrocarbon radical by the sulphur atom and not by the oxygen, as in sulphites, thus:



Ethyl sulphonic acid.



Ethyl sulphite.

They are obtained by oxidation of mercaptans with nitric acid:

$$\underset{\text{Ethyl mercaptans.}}{C_2H_5 . SH} + 3O = \underset{\text{Ethyl sulphonic acid.}}{C_2H_5 . SO_2 . OH}$$

They are strong acids, which unite with metals instead of the hydrogen of hydroxyl, forming salts like potassium ethyl sulphonate, $C_2H_5 . SO_2 . OK$.

Mercaptols (*thioketones*) are formed by the union of ketones and mercaptans:

$$\underset{\text{Acetone.}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CO} + \underset{\text{Ethyl mercaptan.}}{\begin{matrix}C_2H_5 . SH\\C_2H_5 . SH\end{matrix}} = \underset{\text{Ethyl mercaptol.}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}C_2H_5S\\C_2H_5S\end{matrix}} + H_2O$$

When a mercaptol is oxidized the product is a *sulphone*, such as *sulphonmethane* "sulphonal" and *sulphonethylmethane* "trional."

Sulphonmethanum (*Diethylsulphone-dimethylmethane*).—This is formed by oxidizing ethyl mercaptol with potassium permanganate:

$$\underset{\text{Ethyl mercaptol.}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}C_2H_5S\\C_2H_5S\end{matrix}} + 4O = \underset{\text{Sulphonal.}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}C_2H_5SO_2\\C_2H_5SO_2\end{matrix}}$$

It is obtained in colorless, tasteless prismatic crystals, sparingly soluble in cold water or cold alcohol, but quite soluble in hot water or hot alcohol. It is used as a hypnotic, having the same properties as paraldehyd, though more uncertain because of its insolubility in water. Dose: 20 to 40 gr. (1.25–2.50 gm.).

Toxicology.—The symptoms due to excessive doses are: Stupor, insensibility, sometimes preceded by convulsions; the breathing

is irregular, pulse weak, and skin cyanotic. Death may be due to failure of respiration or to suppression of urine. In lingering cases the urine is red from the hematoporphyrin of dissolved blood. The sulphonal *habit* has caused this symptom with albuminuria, eruptions, and impairment of mind and locomotion. Chronic poisoning from long-continued small doses is attributable to the slow elimination by the kidney, causing a cumulative action.

Fatal Dose and Period.—Death has been caused by 30 gr. (1.94 gm.), yet recovery after ninety hours of sleep has followed a dose of 3 oz. (93 gm.). A fatal result in a few hours or days would probably follow 75 gr. (4.85 gm.).

Treatment.—The stomach should be evacuated with a siphon tube, using hot water, and the intestines emptied with purgatives. Hypodermic injections of strychnin are useful to sustain the heart and respiration.

Detection.—Owing to its remarkable stability, urinary or post-mortem isolation is not difficult. It is accomplished by making an alcoholic extract of the material, evaporating, extracting the residue with *hot* water, evaporating, and finally extracting the residue with ether. The tests are applied to the residue of this last extraction.

Test.—Mixed with powdered charcoal and heated in a test-tube, sulphonal is reduced and breaks up into mercaptan (detected by garlicky odor); formic and acetic acids (the vapor reddens litmus paper), and sulphur dioxid (which bleaches paper wet with blue-starch iodid).

Trional, Sulphonethylmethanum, U. S. P. (*Diethylsulphone-methylethylmethane*).—This syllable *tri-* is used because there are three ethyl groups in the compound, while sulphonal has only two:

$$\begin{matrix} C_2H_5 \\ CH_3 \end{matrix} > C < \begin{matrix} SO_2 \cdot C_2H_5 \\ SO_2 \cdot C_2H_5 \end{matrix} .$$

It is a white powder with a faint, bitter taste. It is sparingly soluble in water, and resembles sulphonal in its effects, but is more hypnotic. *Dose:* 7 to 30 gr. (0.5–2 gm.). It has caused death with symptoms like those of sulphonal.

Tetronal (*Diethylsulphone-diethylmethane*).—In this sulphonal compound there are four ethyl groups, each addition of ethyl increasing the hypnotic power:

$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} > C < \begin{matrix} SO_2 \cdot C_2H_5 \\ SO_2 \cdot C_2H_5 \end{matrix} .$$

It is used like sulphonal. Dose: 7 to 30 gr. (0.5–2 gm.).

It is a narcotic poison with symptoms like those of sulphonal.

FATTY ACIDS

The relationship of the fatty acids to other oxygen derivatives of the paraffins is shown in the structural formula of the second member:

C_2H_6	$C_2H_5 . HO$	$CH_3 . CHO$	$CH_3 . COOH$
Ethane.	Ethyl alcohol.	Acetic aldehyd.	Acetic acid.

In another place (p. 410) are the equations for the stages of oxidation from an alcohol to an acid by way of an aldehyd. The aldehyd group, —COH, receiving an addition of oxygen, becomes —COOH, *carboxyl*, and the reactions of the substance change from those of an aldehyd to those of an acid. As the higher members of the acid series are components of animal and vegetable fats, the entire class is called *fatty*, or *aliphatic.*

The first acid, *formic*, H . COOH, has an atom of hydrogen which does not ionize joined to the carboxyl, which contains another atom of hydrogen that is ionizable. Like the lower members of this large series it is a volatile liquid, miscible with water, and having a strong acid reaction. In the succeeding members the non-ionizable hydrogen is replaced by an *alkyl* radical, such as methyl (CH_3) or ethyl (C_2H_5), the molecular weight increasing by CH_2, the boiling-point rising and the specific gravity falling as they ascend. The higher compounds are light, solid, waxy substances without pungent odor, insoluble in water and having very little acid property.

The hydrogen of carboxyl only is replaceable by metals or basic radicals, forming salts. If replaced by an alcoholic radical, the product is called an *ester*. The basicity of an organic acid is in accordance with the number of carboxyl groups it contains. The fatty acids are monobasic, but some other organic acids are dibasic and some are tribasic, forming normal acid, and basic salts. Sometimes the basicity is indicated by a formula which sets apart the hydroxyl, all the remainder being called the *acid radical*; thus, C_2H_3O is called *acetyl* when acetic acid is written C_2H_3O . HO. The general formula for the fatty acids is C_nH_{2n+1} CO . OH.

Fatty acids.		Melts at C. F.	Occurs in
Formic,	H . COOH	8.3° (47°)	Nettles and ants.
Acetic,	CH_3 . COOH	16.5° (62°)	Organic decompositions, vinegar.
Propionic,	C_2H_5 . COOH	—24° (—11.2°)	Urine, sweat.
Butyric,	C_3H_7 . COOH	—4° (24.8°)	As glycerid in butter.
Valeric,	C_4H_9 . COOH	—16° (3.2°)	Valerian plant.
Caproic,	C_5H_{11} . COOH	—2° (28.4°)	As glycerid in butter.
Palmitic,	$C_{15}H_{31}$. COOH	62° (143.6°)	As glycerid in palm oil, solid fats.
Stearic,	$C_{17}H_{35}$. COOH	69° (158°)	As glycerid in stearin, lard, tallow.

Nine acids of no medical importance come between caproic and palmitic. The higher members end in *melissic acid*, $C_{29}H_{59}COOH$, found in beeswax.

Formic Acid.—This was first observed in the stinging liquid ejected by the ant (*formica*). It is also found in the stings of the nettle. When carbon monoxid is passed over gently heated potassium hydroxid, potassium formate is obtained:

$$CO \quad + \quad KOH \quad = \quad H.COOK.$$

The acid is set free by distilling the formate with sulphuric acid. The usual method of preparing it is by heating oxalic acid with glycerin. The formic acid at once combines with the glycerin, which readily gives it up on distillation. Oxalic acid has two carboxyl groups and breaks up as shown in the formula:

$$\begin{matrix} COOH \\ | \\ COO.H \end{matrix} \quad = \quad H.COOH \quad + \quad CO_2.$$

Proof that formic acid is closely related to carbonic acid is found by the action of carbonic-acid water on potassium:

$$2H_2CO_3 \quad + \quad 2K \quad = \quad \underset{\text{Potassium formate.}}{K.CO_2H} \quad + \quad \underset{\text{Potassium bicarbonate.}}{KHCO_3} \quad + \quad H_2O.$$

Properties.—Formic acid is a colorless, volatile liquid with a peculiar pungent odor, marked acid properties, and highly irritating local effects.

Tests.—Its powerful deoxidizing action enables it to precipitate metallic silver from warm ammoniacal solutions of the oxid (see *Tollen's reagent*, p. 411). This reducing power is due to the aldehyd group shown in its structure $\begin{matrix} O \\ H \end{matrix}\!\!>\!C-OH$. The other fatty acids are not reducing agents because they do not have the aldehyd group seen in the formic-acid formula. Heated with concentrated sulphuric acid, H_2O is abstracted, freeing CO. This proves that carbon monoxid is an anhydrid of formic acid:

$$CH_2O_2 \quad = \quad H_2O \quad + \quad CO.$$

Acetic acid, $CH_3.COOH$, is so readily formed by natural fermentations that its general properties have been known from the earliest times. Other substances discovered later to have a similar sharpness in taste were given the name *acids*, derived from the same root word. Its synthesis starts with the action of iodin on methane, making methyl iodid CH_3I. In the presence of potassium cyanid this changes to methyl cyanid. Thus:

$$CH_3I \quad + \quad KCN \quad = \quad CH_3.CN \quad + \quad KI.$$

Boiling methyl cyanid with a dilute mineral acid causes it to react with water and yield acetic acid and ammonia:

$$\underset{\text{Methyl cyanid.}}{CH_3 . C \equiv N} + \underset{\text{Water.}}{\begin{matrix} H\ OH \\ H_2\ O\end{matrix}} = \underset{\text{Acetic acid.}}{CH_3C \begin{matrix} \diagup OH \\ \diagdown\!\!\diagdown O\end{matrix}} + NH_3.$$

The above series of reactions constitutes strong proof that the structural formula of acetic acid must include methyl, CH_3, and hydroxyl associated with carbonyl in the formula—

$$-C\begin{matrix}\diagup OH \\ \diagdown\!\!\diagdown O\end{matrix}.$$

Vinegar Method.—Acetic acid is produced on a large scale in vinegar making. Oxidation of ethyl alcohol results from the influence of a microscopic unicellular plant, *Mycoderma aceti*, which in large masses is called *mother of vinegar.* To facilitate the process of conveying oxygen from the air the natural alcoholic liquor, weak wine, cider, or beer is made to trickle slowly through a ventilated cask over shavings already wet with old vinegar.

Pyroligneous Method.—Among the products of dry distillation of wood are methyl alcohol (*wood spirits*) and acetic acid. The acid is fixed with lime, forming calcium acetate, the other volatile products being distilled off. Distilled with sulphuric acid, the acetic acid separates in the distillate. By repeated distillations and freezing this is purified and freed from water to make *anhydrous* acetic acid.

A little water remains (not more than 1 per cent.) in the commercial acid known as *glacial acid* or *acidum aceticum glaciale.* This is a colorless crystalline solid with an irritating odor, melting at 15° C. (59° F.) to form a strongly acid liquid soluble in water, alcohol, and ether.

Acidum aceticum, U. S. P., contains only 36 per cent. of the anhydrous acid, and *acidum aceticum dilutum*, U. S. P., has 6 per cent.

Vinegar.—In the household a mixture containing from 3 to 6 per cent. of acetic acid is commonly used. The flavor and the color of the vinegar varies somewhat according to its source—wine, cider, beer, or an artificial mixture of essences and coloring matter with dilute acetic acid. Should mineral acids be used as adulterants, they can be detected by the tests mentioned in other places.

Tests for Acetic Acid.—It has a characteristic odor. When heated with alcohol and sulphuric acid it develops the agreeable odor of ethyl acetate. With ferric chlorid it yields a deep red color

which, when boiled, changes to a red-brown precipitate of ferric subacetate.

Chloracetic Acids.—One, two, or all three hydogen atoms in the methyl group of acetic acid may be substituted by chlorin, making the three acids *monochloracetic*, $CH_2ClCOOH$; *dichloracetic*, $CHCl_2COOH$, a colorless liquid used in medicine; and *trichloracetic*, U. S. P., CCl_3COOH, a crystalline substance used as a reagent for albumin. It is deliquescent, has a pungent odor, and is soluble in water, alcohol, and ether. It is a local caustic used to destroy warts and other cutaneous growths.

Butyric Acid.—Two isomeric forms are known of the formula C_3H_7COOH. *Normal butyric acid* occurs in animals and vegetables, sometimes free, but more often as an ester with glycerin. This ester, *butyrin*, is characteristic of butter, from which butyric acid is set free by the rancid fermentation. This acid gives the rancid odor and flavor. When milk sours, lactose is converted into lactic acid by the lactic ferment from various bacteria.

$$\underset{\text{Lactose.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Lactic acid.}}{4C_3H_6O_3}$$

By adding decaying cheese the lactic acid is broken up by the butyric ferment secreted by some putrefactive bacteria:

$$\underset{\text{Lactic acid.}}{2C_3H_6O_3} = \underset{\text{Butyric acid.}}{C_4H_8O_2} + 2CO_2 + 2H_2.$$

Butyric acid is a thick, sour, colorless liquid, smelling like stale perspiration or rancid butter. It mixes with water in all proportions and boils at 163° C. (325.4° F.).

Valeric Acid ($C_4H_9 \cdot COOH$).—Of the four isomeric forms known, two of them occur in the plants *valerian* and *angelica root*, and the mixture obtained by distillation of valerian is the valeric acid used in medicine. This is an oily liquid boiling at 174° C. (345.2° F.) and forming valuable medicinal salts—the valerates of zinc, ammonium, iron, and quinin.

Palmitic acid, $C_{15}H_{31}COOH$, and **stearic acid,** $C_{17}H_{35} \cdot COOH$, occur abundantly in animal and vegetable fats as glycerin esters —*palmitin* and *stearin*. In stearin candle-making these are prepared on a large scale. They are waxy, colorless solids, melting respectively at 62° C. (143.6° F.) and 69° C. (156.2° F.). They are soluble in alcohol and ether, but insoluble in water.

Margaric acid, $C_{16}H_{33}COOH$, does not occur in nature, though the name was formerly given to a mixture of palmitic and stearic acids. It is now reserved for an acid which is prepared artificially.

ORGANIC ACIDS, NOT FATTY

Oleic acid, U. S. P., $C_{17}H_{33} . COOH$, belongs to the acrylic acids, which differ from the fatty acids as the olefins from the paraffins. It is usually found in plants and animals, associated with palmitic and stearic acids as glycerin esters.

In the process of soap-making this acid is produced from fats. The other acids crystallize, leaving oleic acid as an oily liquid at temperatures above 14° C. (57.2° F.).

Oxalic Acid, U. S. P., $(H_2C_2O_4)$.—Glycol, $C_2H_4 . (OH)_2$, has been described (p. 403) as a dihydric alcohol containing two hydroxyl groups. As a *primary* alcohol it yields on oxidation an acid with one carboxyl group—glycollic, $CH_2(OH)COOH$, and a remaining alcohol group, CH_2OH, thus forming a hydroxy- or *alcohol-acid*. Another acid is formed when it is more completely oxidized with two carboxyl groups, oxalic acid, $2(COOH)$:

$$\underset{\text{Glycol.}}{\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}} + 2O_2 = \underset{\text{Oxalic acid.}}{\begin{array}{l} COOH \\ | \\ COOH \end{array}} + 2H_2O.$$

It is dibasic, making two series of salts, neutral and acid oxalates, which are fully discussed in another place (p. 200).

Succinic Acid, $H_2C_4H_4O_4$.—There are two isomers of this acid namely:

$$\text{Ordinary succinic } \begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array} ;\ \text{isosuccinic } \begin{array}{l} CH(COOH)_2. \\ | \\ CH_3 \end{array}$$

They are distinguished by heating to 150° C. (302° F.); the ordinary acid is not changed, but the isosuccinic splits to form propionic acid and carbon dioxid. A trace of the ordinary acid is produced in alcoholic fermentation and is also found in the gastric contents when mould is present.

Detection.—The gastric contents are shaken with ether, which is then separated by a funnel and evaporated to dryness. The residue is dissolved in weak ammonia, the excess of ammonia then boiled off, and the neutral solution remaining is added to dilute ferric chlorid; a brown-red precipitate is formed by succinic acid.

Glutaric Acid, $COOH(CH_2)_3COOH$.—*Normal pyrotartaric*, the next member of the homologous series with succinic acid, crystallizes in large plates, soluble in water. It forms an amino-acid (glutamic) which is a constituent of proteid matter.

HYDROXY- OR ALCOHOL-ACIDS

Lactic Acid, U. S. P., ($C_3H_6O_3$) (*Hydroxypropionic Acid*).—It has been stated above that this acid is the characteristic product of the lactic fermentation occurring in sugar, starch, and other carbohydrates, when animal nitrogenous matter is present (see Butyric Acid, p. 421). It can be prepared also by oxidizing propyleneglycol with nitric acid. Several acids are known of the same molecular formula, and three are stereo-isomeric, $CH_3CH<^{OH}_{COOH}$. These are distinguished apart by differences of crystalline structure, solubility, and effects on polarized light. This last property gives the names, *inactive*, *dextro-*, and *levo-rotatory lactic acids*.

Ordinary Lactic Acid (*Inactive to Polarized Light*).—This is the acid present in sour milk (see p. 560). The lactic acids are thick, sour liquids, miscible with water and alcohol in all proportions.

From organic mixtures lactic acid can be separated by first acidifying with sulphuric acid and shaking with ether. This ethereal extract, underlaid with solution of ferric chlorid, gives at the line of contact a yellow band. It is a monobasic acid, forming metallic salts and esters known as *lactates*. It contains the alcoholic group, $>CH\,.\,OH$ and shows many of the reactions of a secondary alcohol.

Sarcolactic acid ($C_3H_6O_3$) (*paralactic acid, dextrolactic acid*) occurs in the juices of muscles, and can be prepared from extract of meat. The constitution and chemical behavior are the same as those of ordinary lactic acid, but optically this acid is active, turning the polarized ray to the right. The acid rotating to the left, *levolactic*, is produced by a special ferment working on cane-sugar.

Oxybutyric Acid.—In the oxidation of secondary normal butyl alcohol, (p. 401), the first group only (CH_3) is oxidized to COOH. This must always be at either end of the chain to give the carbon atom the three valences needed for the $-C<^{OH}_{O}$. The alcohol hydroxyl may be attached to any of the remaining C atoms, and thus make it a hydroxyacid or oxyacid. The relative position of the HO group in the three possible oxybutyric acids are indicated below by the Greek letters (α) alpha, (β) beta, (γ) gamma.

COOH	COOH	COOH	COOH
|	|	|	|
CH_2	α CHOH	α CH_2	α CH_2
|	|	|	|
CH_2	β CH_2	β CHOH	β CH_2
|	|	|	|
CH_3	γ CH_3	γ CH_3	γ CH_2OH
Butyric acid.	α Oxybutyric acid.	β Oxybutyric acid.	γ Oxybutyric acid.

The levo beta oxybutyric acid is especially interesting, as it is found associated with diacetic acid and acetone in the blood and urine of severe cases of diabetes. It is a factor in the *acidosis* of diabetic coma.

Test.—Detection in the urine is not easy. Dependence is placed usually on the red ferric chlorid reaction given by its constant companion, diacetic acid. One method is to remove dextrose from the urine by fermentation and then estimate the remaining oxybutyric acid by its levorotation of the ray in the polariscope (p. 61).

Tartaric acid, U. S. P., $C_4H_6O_6$, is a constituent of a large number of plants, occurring in many fruits, such as the berries of the mountain ash, and particularly in grapes. In the making of wine the secondary fermentation in the cask causes the formation of a dark red deposit. This deposit, *argol*, or *crude tartar*, is an impure potassium bitartrate. By solution and recrystallization this is purified and then treated with chalk and calcium chlorid to form a precipitate of calcium tartrate. With dilute sulphuric acid the calcium is removed as insoluble sulphate and tartaric acid is left in solution. The solution is filtered off and crystallized in large colorless prisms without odor, but with a sour taste. This is the *ordinary tartaric acid* (*dihydroxy-succinic acid*), which is dibasic, forming neutral and acid tartrates, such as monopotassium tartrate, sodium potassium tartrate, and antimony potassium tartrate.

By synthesis it can be built up in such a way as to indicate that its constitution consists of two similar groups united, as a dihydroxy-dicarboxylic acid:

$$\begin{array}{l}\mathbf{C}\mathrm{H(OH)COOH}\\ |\\ \mathbf{C}\mathrm{H(OH)COOH}\end{array}.$$

The two dark carbon atoms are linked together at one point, but have different atoms or groups at other points.

When substances of the composition $C_4H_6O_6$ having similar chemical properties are studied by polarized light, four different isomeric modifications are recognized: *dextrotartaric*, *levotartaric*, *mesotartaric*, and *racemic acids*. These examples of optic activity are regarded as proofs of the rule that it depends upon molecular asymmetry.

Stereo-isomerism is isomerism explained by differences of arrangement in space of three dimensions. Ordinary tartaric acid crystallized from grape juice rotates the polarized ray to the right, but the remaining juice contains another acid, *racemic*, with the same formula, $C_4H_6O_6$, and identical chemically, but different

physically, its solution being inactive to polarized light. The sodium-ammonium salts of these acids have the same composition, $Na(NH_4)C_4H_4O_6$, and the same difference optically as their acids. The crystalline form of the tartrate is shown in *D* (Fig. 78) while the racemate is found to crystallize in two forms, one like *D*, the other like *L*, each the reflected image of the other.

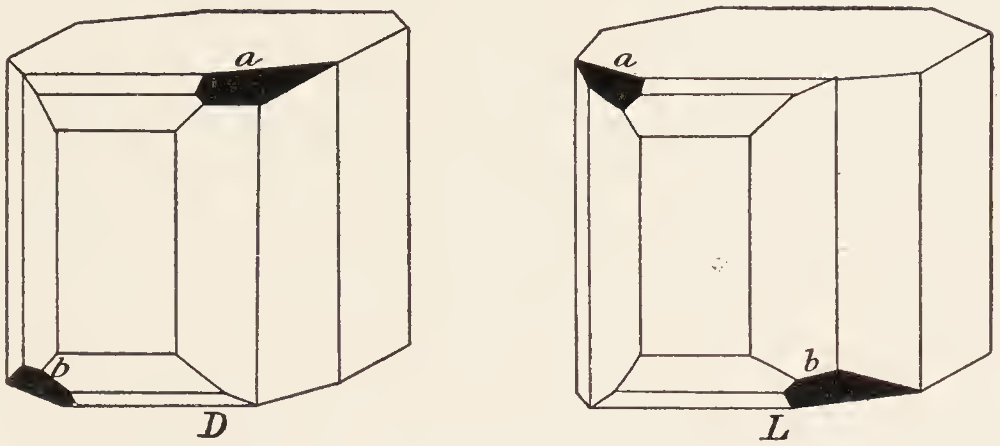
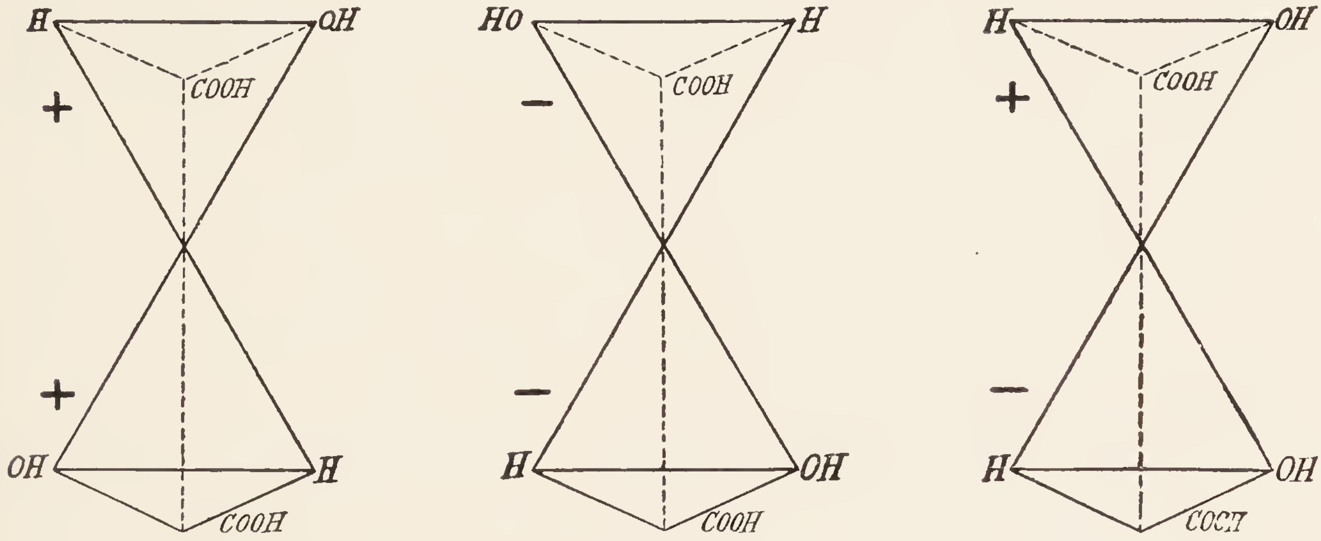


FIG. 78.—Isomeric salts of tartaric acid: *D*=dextrorotatory; *L*=levorotatory.

The differences are in the arrangement of the small faces (*a*, *b*), darkened in the figure. When the crystals of each kind are set apart, separately dissolved, and tested with the polariscope, the solution of *D* is found to be *dextrorotatory*, and that of *L*, *levorotatory*. There is then a dextrotartaric acid and a levotartaric acid. If these solutions of equal concentration be mixed, they



D-tartaric acid. *L*-tartaric acid. Mesotartaric acid.

FIG. 79.—Isomeric forms shown by tetrahedral models.

neutralize each other optically and *racemic acid* ($D + L$ tartaric acid) is produced.

From dibromsuccinic acid a fourth isomer, λ, *mesotartaric acid*, is obtained. This is optically inactive, like racemic acid, but can not be split into the right- and left-handed acids.

A study of the optically active substances shows that this property depends upon the presence in the molecule of an asymmetric carbon atom—that is, one which is joined immediately to

four *different* atoms or groups. Each of the four is supposed to be at the end of one of four different lines drawn from this carbon atom at the center of an imaginary tetrahedron to the corners.

If two tetrahedral models, representing two compounds, are manipulated it is found that the two asymmetric carbon atoms are capable of three distinct arrangements, corresponding to the three tartaric acids, the fourth being an externally compensated mixture of two others (Fig. 79).

Three of the forms may be represented by the three different graphic formulas below, in which the solid black letter **C** stands for an asymmetric carbon atom.

$$
\begin{array}{ccc}
\begin{array}{c}
COOH \\
| \\
H-\mathbf{C}-OH \\
| \\
OH-\mathbf{C}-H \\
| \\
COOH
\end{array}
&
\begin{array}{c}
COOH \\
| \\
OH-\mathbf{C}-H \\
| \\
H-\mathbf{C}-OH \\
| \\
COOH
\end{array}
&
\begin{array}{c}
COOH \\
| \\
H-\mathbf{C}-OH \\
| \\
H-\mathbf{C}-OH \\
| \\
COOH
\end{array}
\end{array}
$$

D-tartaric acid. *L*-tartaric acid. Mesotartaric acid.

Using tetrahedral models for the black-letter carbon atoms, these compounds are represented in the diagrams above (Fig. 79), where the groups are arranged in space of three dimensions, thus giving a perect illustration of *stereo-isomerism.*

Citric acid, U. S. P., $C_6H_8O_7$, is found free in the juice of the lemon, orange, gooseberry, raspberry, and many other sour fruits. It is prepared by boiling lemon juice and neutralizing with calcium carbonate. The calcium is fixed by sulphuric acid, leaving free citric acid in solution. The filtrate on evaporation deposits large colorless prismatic crystals, freely soluble in water.

It is extensively used in pharmacy to prevent the precipitation of ferric hydroxid and other hydroxids from their salts. The solutions, thickened by evaporation and dried on glass plates, yield the brilliant scales which have given the name *scale preparations* to these compound tartrates and citrates.

The synthetic reactions of this acid show that it is a hydroxytricarboxylic acid of the constitution:

$$
\begin{array}{l}
CH_2 \cdot COOH \\
| \\
C(OH) \cdot COOH \\
| \\
CH_2 \cdot COOH.
\end{array}
$$

Being tribasic, it forms three classes of salts, in which one, two, or three hydrogen atoms of the carboxyl groups are replaced by metals.

Tests for Tartaric and Citric Acids.—Calcium chlorid yields a white precipitate with both. Boiling does not change citrates,

but darkens tartrates. Potassium permanganate decolorizes tartrates, but turns citrates green.

KETONE-ACIDS

These acids contain the CO of ketones as well as the COOH of acids. The only one of medical interest is aceto-acetic acid, or **diacetic acid,** $CH_3CO \cdot CH_2COOH$, which is associated with acetone in the urine and blood of severe cases of diabetes. It is a colorless syrupy liquid. It is believed to be derived in the blood from β-oxbutyric acid $CH_3 \cdot CHOH \cdot CH_3 \cdot COOH$ by oxidation. It is called diacetic acid because two molecules of acetic acid are united in it by the elimination of H_2O, thus:

$$CH_3 \cdot CO\boxed{OH-H}CH_2 \cdot COOH.$$

The beta-ketone acids are all unstable, some of them decomposing at ordinary temperature (p. 626). Thus, aceto-acetic acid decomposes into acetone and carbon dioxid:

$$CH_3 \cdot CO \cdot CH_2CO \cdot OH \quad = \quad CH_3 \cdot CO \cdot CH_3 \quad + \quad CO_2.$$

Test.—Having acidulated 50 c.c. of urine with sulphuric acid, it is shaken with an equal volume of ether. The ether separated is shaken with a small quantity of dilute solution of ferric chlorid. A red or violet color in the reagent indicates aceto-acetic acid.

Fallacy.—Antipyrin, salicylates, and other synthetic aromatic drugs give a blue-red or purple color to ferric chlorid, but the color is deepened by warming, whereas the diacetic-acid red ether disappears or is greatly lessened (Plate 8, Fig. 6).

FATS AND FATTY OILS

Tallow is the solid fat obtained from beef and mutton suet by expression when kneaded in a muslin bag under hot water. *Lard* is hog fat treated by a similar process. *Fatty oils* are obtained by pressing the seeds or fruits of cotton, olive, linseed, and palm. When treated with superheated steam all of them absorb water and break up into *glycerin* (glycerol) and the acids, oleic, palmitic, and stearic. Distilled in the hot steam, these pass over and are collected in the receiver with the acids in a semisolid mass, floating on the dilute glycerin.

$$\text{Fat} + \text{water at } 200^\circ \text{ C.} = \text{glycerin} + \text{acid.}$$

To express the movement of the atoms the following equation is used, the fat being *tristearin:*

$$\begin{array}{llllll} CH_2.O.OC.C_{17}H_{35} & & & CH_2.OH & & HO.OC.C_{17}H_{35} \\ | & & & | & & \\ CH\ .O.OC.C_{17}H_{35} & + 3H_2O & = & CH\ .OH & + & HO.OC.C_{17}H_{35} \\ | & & & | & & \\ CH_2.O.OC.C_{17}H_{35} & & & CH_2.OH & & HO.OC.C_{17}H_{35}. \\ \text{Tristearin} & & & \text{Glycerin} & & \text{Stearic acid} \\ \text{(1 molecule)} & & & \text{(1 molecule).} & & \text{(3 molecules).} \end{array}$$

Glycerin has already been described as a tri-acid base, under the class of Trihydric Alcohols (p. 402); its formula is $C_3H_5(OH)_3$, or *glyceryl trihydroxid.* The fats are sometimes called *glycerids*, *glycerin esters*, or *ethereal salts.* They are named after the acids forming them, as *tripalmitin* (or glyceryl tripalmitate), *tristearin*, and *triolein.* The firm solid fats, such as tallow, get their hardness at ordinary temperatures from their large proportion of tristearin and tripalmitin. Those that are soft, like lard, have a large proportion of olein, and the liquid oils are composed chiefly of that constituent.

Saponification.—The fats decompose more readily by the action of alkalis than by hot water alone. The acids leave the weak base glycerin to join the alkali metals, forming *soaps.* A soap then is *a salt containing an alkali metal united with oleic, palmitic, or stearic acids.* They remain dissolved in water until common salt is added to make them insoluble, when the curds of soap rise to the surface. The glycerin is left dissolved in the liquid with the mineral salt.

$$C_3H_5\begin{cases} O.C_{18}H_{35}O \\ O.C_{18}H_{35}O \\ O.C_{18}H_{35}O \end{cases} + 3KOH = C_3H_5\begin{cases} OH \\ OH \\ OH \end{cases} + 3KOC_{18}H_{35}O.$$

Glyceryl stearate (stearin). Glycerin. Potassium stearate (soft soap).

When sodium replaces the hydrogen of stearic, palmitic, and oleic acids the product is *hard soap* (*sapo*, U. S. P.). If potassium be the alkaline metal, then *soft soap* (*sapo mollis*, U. S. P.) is the product.

From this first process of splitting up a fatty ester of glycerin with a metallic hydroxid the term saponification was extended to the *decomposition of esters by alkalis*, even when the product was not a soap. Thus:

$$\underset{\text{Ethyl sulphate.}}{(C_2H_5)_2SO_4} + 2KOH = \underset{\text{Alcohol.}}{2C_2H_5OH} + K_2SO_4.$$

Experiment 1.—Make a solution of potassium hydroxid, 10 gm., in 100 c.c. of water and put in a beaker with 25 gm. of tallow. Boil and stir about half an hour until oil globules disappear from the surface. The homogeneous liquid is a mixture of glycerin, soap, and potassium hydroxid. Add a solution of 15 gm. of sodium chlorid in 75 c.c. of water and boil again. The soft potash soap changes to hard sodium soap, which separates and floats on the briny liquid.

Experiment 2.—Skin off the sodium soap or use a piece of ordinary soap; dissolve in water, with the aid of alcohol. Add solution of calcium chlorid; a white precipitate of insoluble lime soap separates. Soaps of alkalis are the only ones soluble.

Hydrolysis is a term for the analogous *decomposition when water is absorbed* and not the alkaline hydroxid. It implies that the breaking up of one compound into two or more is consummated by the participation in the process of the elements of water as in the splitting of fats by superheated steam (p. 403). Thus:

$$\underset{\text{Ethyl acetate.}}{C_2H_5 \,.\, C_2H_3O_2} + H_2O = \underset{\text{Acetic acid.}}{C_2H_4O_2} + \underset{\text{Alcohol.}}{C_2H_5OH}$$

Hydrolysis may be brought about by an enzym of the pancreatic juice known as *steapsin*. The process is sometimes referred to as *hydrolytic cleavage*.

Experiment 3.—Put in a test-tube 5 c.c. of oil and a few drops of oleic acid, add 10 drops of a strong solution of sodium carbonate and shake well. The sodium and the free acid unite to make a soap which envelops the fat globules so that they do not coalesce, but make a permanent *emulsion*.

Butter.—The *butter-fat* of milk is a complex mixture of glycerids, characterized by a relatively larger amount of lower volatile fatty acids. When decomposed by hydrolysis it yields about 95 per cent. of fatty acids, 85 to 90 per cent. of which are the non-volatile, insoluble, higher acids—stearic, palmitic, oleic, myristic—and the remainder, 5 to 10, is made up of the volatile, soluble acids—butyric, caproic, caprylic, and capric. No other fat yields so large a percentage of volatile acids when distilled with water.

Oleomargarin is an imitation of butter in color, odor, and taste. It is manufactured from beef suet. The beef fat is minced fine, heated by steam, and at a certain temperature put under pressure. A yellow oil (*oleo oil*) exudes and solid *stearin* remains. The oleo oil is churned with milk to get the butter flavor and colored with artificial *butter yellow*. When the process is carefully conducted a product is obtained which may not be so easily digested as butter, but which is wholesome and nutritious. *Butterin* and *suin* are of similar manufacture, using the fat not only of beef, but also of mutton; and sometimes they contain lard and cotton-seed oil.

Properties of Fats.—When pure, the fats are without odor or color, leave a greasy stain on paper, are lighter than water, with which they do not mix. They are soluble in ether, chloroform, carbon disulphid, benzol, alcohol, etc. When the solid fats are dissolved in ether or chloroform and evaporated on the slide of a microscope, characteristic crystals are seen. As found in nature,

they have taste, odor, and color, due to more or less impurity. On standing they become *rancid*—that is, they acquire an unpleasant smell and taste and an acid reaction. This is due to the action of oxidizing ferments, which in the case of butter may be prevented or retarded by the admixture of antiferments, such as boric acid. Rancidity is sometimes corrected and the butter "renovated" by heating with solution of sodium carbonate.

Fats and fatty acids are extracted from other material by shaking with ether, which dissolves them, but not the mineral salts, proteins, or carbohydrates. A separating funnel lets the aqueous material run off first, retaining the ether.

Tests.—1. Fats are the only substances that are stained by the alcoholic solution of red Sudan III.

2. Osmic acid, in 1 per cent. aqueous solution, stains olein black, but does not stain the other fats. Olein is always present in animal fats.

3. Triturate well in a mortar a small amount each of olive oil and potassium bisulphate. Carefully dry a test-tube, put into it the trituration mixture, and cautiously heat. An irritating odor of burning grease is perceived due to *Acrolein* developed from the glycerol (p. 403).

Fats in the Body.—A certain percentage of fats is present in almost all our food-stuffs. They make up nearly all of the weight of olive oil, cream, butter, bacon, and the fatty tissue of ordinary meats. The fundus of the stomach secretes a lipase which can split emulsified fat of milk. Fats are not completely digested until they reach the small intestine, where they undergo hydrolytic cleavage (p. 429) by the action of a pancreatic enzym, *steapsin*, and another *lipase* of the bile into glycerin and the fatty acids. Some of the free acid unites with the sodium of the alkaline bile and intestinal juices to form a soap.

This soap emulsifies the rest of the fat, hastening the action of the steapsin upon it, and promoting its absorption. It is a growing opinion that the fat is all split first and passes into the intestinal cells in solution as soap, glycerin, and free acid, which during transmission are recombined into molecular fat by the cells, reversing the reaction and splitting off the sodium. Some of the stored fat of adipose tissue in the body is derived from sugar and some from proteid substances, beside what may be obtained from fatty foods. Most of the fat of food is oxidized to CO_2 and H_2O in the tissue cells as fast as it comes to them, affording molecular and chemical energy and maintaining the normal temperature. Being rich in carbon, fat is very combustible and liberates a large amount of heat. The stored fat is a reserve of potential energy brought into use in wasting diseases attended by failure of nutrition.

Waxes.—The class of which beeswax is a member does not have glycerin as a component. It includes the esters of monatomic alcohols, such as melissyls up to C_{30} united with higher fatty acids up to C_{18}.

Lipoids are fat-like substances extracted from the tissues with ether or alcohol. They comprise the cholesterins (p. 567), cerebrosids, and phosphatids, or phospholipins, to which class belongs lecithin (p. 525). The *cerebrosids* are extracted with alcohol from white nervous tissue, contain nitrogen, but no phosphorus, and are allied to glucosids (p. 446). On hydrolysis *cerebrin* yields the carbohydrate galactose, fatty acids, and complex bases.

ESTERS

Esters are *compounds containing an organic radical combined with an acid radical, which may be either inorganic or organic.*

In the presence of acids the alcohols behave like metallic hydroxids replacing acid hydrogen with a radical, with water as a by-product. These are sometimes called *ethereal salts*, but a better name is *esters*, as they do not dissociate, after the manner of true salts. Mention has been made of the first reaction between sulphuric acid and alcohol, producing ethyl hydrogen sulphate, $C_2H_5HSO_4$, and water (p. 405), the intermediate products in the conversion of alcohol into ether. This compound, also called *ethyl sulphuric acid* and *sulphovinic acid*, has an acid reaction and acts like a monobasic acid, since it retains one atom of replaceable hydrogen. The formula, $SO_2<\begin{matrix}OC_2H_5\\OH\end{matrix}$, is typic of a class known as *ethereal sulphuric acids*, in which the radical (R) is linked to the sulphur by an oxygen atom, while in sulphonic acids the radical is directly united to the sulphur atom. This difference of constitution is indicated as follows:

$$\begin{matrix}O\diagdown & & \diagup OR\\ & S & \\ O\diagup\!\!\!\diagup & & \diagdown OH\end{matrix} \qquad\qquad \begin{matrix}O\diagdown & & \diagup R\\ & S & \\ O\diagup\!\!\!\diagup & & \diagdown OH\end{matrix}$$

Ethereal sulphuric acid. Sulphonic acid.

For the hydrogen of the $-OH$, metals and bases can be substituted, thus constituting a large class known as *ethereal sulphates*, as sodium ethyl sulphate, $SO_2<\begin{matrix}OC_2H_5\\ONa\end{matrix}$.

It is the characteristic of sulphanion, $(SO_4)''$, to form with barium, $Ba^{\cdot\cdot}$, an insoluble $BaSO_4$. As ethyl sulphuric acid forms no precipitate with barium chlorid, its dissociation must be into the hydrogen cation and a complex anion, thus: $H^{\cdot}(C_2H_5SO_4)'$.

In order to precipitate an ethereal sulphate with barium chlorid this complex anion is first broken up by boiling with hydrochloric acid to liberate $(SO_4)''$ (p. 603).

Ethyl Nitrate ($C_2H_5 . NO_3$) (*Nitric Ether*).—Owing to the heat evolved and explosive violence of the reaction, it is not prudent to make this compound by the direct action of concentrated nitric acid upon alcohol. When urea is present to decompose the nitrous acid formed, the operation is much less violent and the distilled product is ethyl nitrate.

It is a colorless, volatile liquid, with an agreeable fruity odor.

Ethyl nitrite ($C_2H_5 . NO_2$) (*nitrous ether*) can be prepared by the action of nitrous acid on alcohol:

$$C_2H_5OH + HNO_2 = C_2H_5 . NO_2 + H_2O.$$

This is a colorless, volatile liquid, with an odor like that of apples. When 4 per cent. is mixed with alcohol it is employed in medicine as *sweet spirits of niter, spiritus ætheris nitrosi.*

Amyl nitrite ($C_5H_{11} . NO_2$) (*amylis nitris*), prepared by the action of nitrous fumes on amyl alcohol. It is a yellowish volatile liquid, with a peculiar fruity and suffocative odor. It is insoluble in water. The 80-per cent. alcoholic solution is used in medicine. Its vapor explodes when heated to 95° C. (203° F.).

Toxicology.—When inhaled it dilates the arteries, causing flushing of the face and a sense of fulness about the head. It relieves cardiac tension and the painful feelings of angina pectoris. In poisonous doses it produces weakness, nausea, vomiting, thready pulse, stupor, and collapse with cyanosis.

The antidotes are strychnin hypodermically, and digitalis. When swallowed it may be detected in the gastric contents by distillation, carefully protecting the distillate from evaporation. By agitation of the aqueous distillate with ether it may be separated. By heating with potassium hydroxid the amyl nitrite forms amyl alcohol and potassium nitrite. The latter may be identified by the tests for nitrites.

Nitroglycerin ($C_3H_5(NO_3)_3$) (*glyceryl trinitrate, trinitrin, glonoin*) is an ester of nitric acid and glycerin. It is prepared by gradually mixing glycerin with sulphuric and nitric acids. The product is a heavy oil, which is washed thoroughly with water and dried.

Properties.—It is a pale yellow oil of specific gravity of 1.6, with a sweet taste, insoluble in water, soluble in ether, and sparingly soluble in alcohol. It ignites with difficulty by a flame in an open vessel, but when suddenly heated to 250° C. (482° F.) it explodes. Its most remarkable property is that of exploding with violent energy on percussion. The complex molecule con-

taining combustible elements in intimate association with oxygen instantly breaks up into a large volume of mixed gases, CO_2, H_2O, and free N. To make it safer when handled the nitroglycerin is absorbed into an inert infusorial earth, and is then called *dynamite.* This does not explode by pressure or by a simple jar.

When mixed with guncotton (*nitrocellulose*) it is employed as *blasting gelatin.* It enters into the composition of certain forms of smokeless powders.

Medical Uses.—When inhaled nitroglycerin causes aching and a sense of fulness with throbbing in the head. Its effects on heart diseases are like those of amyl nitrite, only intensified and more persistent. By relaxing the peripheral vessels it relieves the high blood-pressure and spasmodic pain of angina pectoris. *Spiritus glycerylis nitratis* is a 1-per cent. alcoholic solution. *Dose:* 1 to 2 min.

Toxicology of Nitroglycerin.—*Powder headache* is a symptom frequently seen in persons employed in the manufacture of the high explosives containing nitroglycerin. One drop applied to the unbroken skin may cause prolonged headache. Criminals give it in whisky to "knock out" the victim.

Symptoms.—Severe headache is constantly present, with giddiness, fulness of the arteries, throbbing of the temples, and muscular weakness. Marked distress is caused by vomiting, diarrhea, and griping pains. The breathing is hurried and difficult; cyanosis and coma soon appear. Habitual exposure and dosing soon induce tolerance.

Fatal Dose.—A few drops of the undilute nitroglycerin would probably be fatal. Death does not usually occur for several hours, even after large doses.

Treatment.—The stomach and bowels should be promptly washed out or evacuated. The symptoms should be treated as they arise.

Postmortem Appearances.—The alimentary tract shows congestion, due to local irritation; the brain and meninges are hyperemic.

Detection.—Nitroglycerin rapidly decomposes after absorption. It must be sought in the vomited matters and contents of the stomach. These are to be shaken out with chloroform or ether. The extract evaporated leaves a residuum of fat and nitroglycerin. Cold alcohol dissolves the nitroglycerin, leaving the fat, and evaporation of the alcohol gives us the material to test.

Tests.—(1) Heated in a capillary tube nitroglycerin explodes. (2) Like all nitrates and nitrites it develops a crimson color when treated with brucin and a drop of concentrated sulphuric acid.

ESTERS OF ORGANIC ACIDS

These resemble one another more closely than do the esters of the diverse mineral acids. They are formed to some extent when an alcohol is treated by an organic acid, such as formic, acetic, or butyric. The process is soon arrested, as the water formed hydrolyzes the ethereal salt, reconverting it into ester, acid, and alcohol, an equilibrium resulting. To remove the water the complete process requires that some dehydrating agent, such as sulphuric or hydrochloric acid, should be present.

When an ester such as ethyl acetate is added to water the process is reversed. Alcohol and acetic acid are formed until all four are present in a certain degree of concentration, which is maintained until a dehydrating agent, such as sulphuric acid, is added. This breaks up the phases of the system in equilibrium by removing the component water. The double arrows of the following equation mean that the movements are opposite in direction when equivalent amounts of the factors are used (p. 83).

$$\text{Alcohol} + \text{Acetic acid} \rightleftarrows \text{Ethyl acetate} + \text{Water.}$$

Ethyl Acetate ($C_2H_5 . C_2H_3O_2$) (*Acetic Ether*).—This is prepared by mixing alcohol, acetic acid, and strong sulphuric acid, and distilling by heat. The distillate is shaken with a strong solution of common salt, to take up the alcohol, and the ethyl acetate rises to the top as a colorless, mobile, oily-looking fluid. It has a pleasant fruit-like smell, and is moderately soluble in water. The fine bouquet of hock wine is due mainly to the small amount of ethyl acetate it contains.

This is a type of the class of ethereal salts which are found naturally in fruits and flowers, giving to them, by varied blendings, the scent and flavor. *Artificial fruit essences* are prepared after processes like that given above for ethyl acetate, and largely sold to flavor ices, syrups, candies, and pastries. *Pear oil* is amyl acetate, *pineapple oil* is methyl butyrate, *wintergreen oil* is methyl salicylate.

CARBOHYDRATES

The term carbohydrate is applied to certain substances composed of carbon, hydrogen, and oxygen, the two latter being in the ratio to form water. The carbon atoms are in an open chain. In this group will be found the most important solid constituents of plants suitable for human food—sugars, starches, dextrins, and cellulose.

For good reasons, substances have been admitted to the group

which are known to contain hydrogen and oxygen in a ratio different from H_2O, such as the sugar rhamnose, $C_6H_{12}O_5$. Some others, such as formaldehyd, CH_2O, and acetic acid, $C_2H_4O_2$, are not named carbohydrate, though they contain carbon and the elements of water.

The termination *-ose* is used to denote membership in the carbohydrates; thus, *dextrose*, *levulose*, *amylose*.

Properties.—Most of the carbohydrates are fermentable with yeast, or easily change to fermentable compounds. They are usually neutral, white, non-volatile, odorless solids, and in solution turn a polarized ray of light from the direct path. The sugars are sweet, reduce metallic oxids, and change by oxidation to saccharic, mucic, or oxalic acids.

Classification.—The modern division of carbohydrates is into simple sugars, compound sugars, and starches, or:

Monosaccharids (*monoses* or *simple sugars*), which cannot be made to yield other sugars by the action of dilute acids (glucose, levulose, pentose, galactose, etc.). About 12 simple sugars occur in nature, all of which, and in addition 40 others, purely artificial, have been made by synthesis in the laboratory.

Disaccharids (*saccharobioses*), which, by boiling with dilute acids, can be made to take up 1 molecule of water and split up into 2 simple sugar molecules (saccharose, maltose, lactose, etc.).

Trisaccharids, which by boiling with acids take 2 molecules of water and split into 3 sugars (raffinose).

Polysaccharids, which are not sugars, but by the hydrolytic action of boiling dilute acids take up 2 or more molecules of water and yield a number of simple sugar molecules (starches, gums, cellulose, etc.).

MONOSACCHARIDS

The structure of the monosaccharids has been determined as that of mixed compounds, which are either alcohols and aldehyds (*aldoses*), or alcohols and ketones (*ketoses*). The aldoses contain the alcohol group, CH_2OH, and the aldehyd group, COH; the ketoses have the same alcohol group and the ketone group CO, linking 2 radicals.

The monosaccharids are called, according to the number of carbon atoms they contain, trioses, $C_3H_6O_3$; tetroses, $C_4H_8O_4$; pentoses, $C_5H_{10}O_5$; hexoses, etc., up to nonoses, $C_9H_{18}O_9$, which have 9 carbon atoms. Only those containing 3 carbon atoms or a multiple of three (trioses, hexoses, nonoses) are capable of alcoholic fermentation or of assimilation by digestive processes. They are neutral, white, sweet, odorless compounds, soluble in water and sparingly so in alcohol. Containing a number of alcoholic groups, they share with aldehyds and ketones a reducing power on

metallic oxids; hence give the familiar reaction of reduction shown by Fehling's, Boettger's, and Nylander's tests (p. 618). Minute traces of any sugar are detected by Molisch's test (p. 477), in which a violet color is developed when the carbohydrate is mixed with a small amount of alpha-naphthol and sulphuric acid. This is due to a combination of alpha-naphthol with the furfuraldehyd formed by the action of sulphuric acid on the sugar. Their solutions acidulated with acetic acid and heated with phenylhydrazin all give yellow crystalline precipitates, called *osazones* (Plate 3). This last reaction separates the sugars from aldehyds, ketones, and all other substances. While all are interesting chemically, to the physician only the hexoses and pentoses have any importance.

The **hexoses,** $C_6H_{12}O_6$, include dextrose, levulose, and galactose. **Dextrose** (*glucose*) is called also *grape sugar*, because it is abundant in grapes and forms the brownish warty masses on raisins. Mixed with levulose (*fructose*) it is widely distributed in the sweet juices of fruits and in honey. Human blood and urine in their normal condition may contain traces, but not more than 0.1 per cent., revealed by very delicate tests. In diabetes mellitus the proportion rises sometimes higher than 5 per cent., and then constitutes the chief phenomenon of disease.

Preparation.—When a solution of starch or other polysaccharid is acidulated with sulphuric or some other mineral acid and boiled, the starch is hydrolyzed and splits up, forming, when dry, the commercial *grape-sugar*, of which 60 per cent. is true glucose. Sometimes the product is not evaporated to dryness, and is a thick, colorless syrup, commercial *glucose*, which contains, besides sugar, some dextrins and nitrogenous bodies.

From both of these products the sulphuric acid is removed in the manufacture by neutralizing with calcium carbonate, which precipitates calcium sulphate. As commercial sulphuric acid often contains traces of arsenic and lead, it is not surprising that glucose made by its aid sometimes causes slow poisoning. Widespread epidemics have resulted from brewing beer with such a glucose (p. 289).

Sulphurous acid is sometimes used to decolorize the syrup, and sulphites may be left in it as a contaminant. These are active antiferments, injurious to the digestion.

Properties.—Dextrose, $C_6H_{12}O_6$, is an *aldose*—that is, it has the behavior of an *aldehyd* and also of a polyhydric *alcohol*. From a sufficient number of experimental data its constitution has been worked out to be $CH_2OH . (CHOH)_4 . COH$.

The ordinary syrup of the grocers is commonly liquid glucose made from starch, decidedly less sweet than the syrups made from cane-sugar. Dextrose by evaporation may be obtained as

hard anhydrous crystals, or another sort with 1 molecule of water of crystallization. It is less soluble and less sweet than cane-sugar, and, unlike that substance, is not charred when warmed with sulphuric acid. Its aqueous solutions placed in the polarizing apparatus are dextrogyrous (hence the name dextrose)—that is, they turn the ray of polarized light toward the right hand, $[\alpha]_D = +52.5°$ (p. 61).

Dextrose, like the aldehyds, is an active reducing agent, precipitating the metal from warm solutions of the salts of silver, gold, and platinum. Its reduction tests (Fehling's, etc.) are given in detail in another place (p. 618). With brewer's yeast its dilute aqueous solutions readily ferment at ordinary temperatures, according to the equation:

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} = \underset{\text{Alcohol.}}{2C_2H_6O} + 2CO_2.$$

In addition to the principal products, ethyl alcohol and carbon dioxid, a trace of amyl alcohol is formed and some glycerin and succinic acid. A weak solution made feebly alkaline and exposed to direct sunlight yields the same products, thereby showing a natural tendency to break up this way, which the zymase of yeast accelerates. With phenylhydrazin acetate and gentle heat it forms fine crystals of phenylglucosazone, which fuse at 205° C. (401° F.) (Plate 3, *a*).

The hydrogen of one of the glucose hydroxyl groups may be replaced by a metal as if the molecule were slightly acidic. Thus, the basic compound *calcium glucosate*, $C_6H_{11}O_5O \cdot CaOH$, formed with calcium hydroxid, which is readily decomposed by carbonic acid.

When oxidized with bromin water, dextrose, $CH_2OH(CHOH)_4$-COH, is changed to monobasic *gluconic acid*, $CH_2OH(CHOH)_4$-$COOH$. More powerful oxidizers, such as nitric acid, produce dibasic *saccharic acid*, $COOH(CHOH)_4COOH$, the last oxidation derivative of dextrose being oxalic acid. In the body the COH group of glucose is not oxidized first to gluconic acid, but the CH_2OH group is oxidized, making glycuronic acid. In the laboratory, by reduction of saccharic acid, the first product is *glycuronic acid*, $COOH \cdot (CHOH)_4COH$, a normal constituent of the body which is eliminated in appreciable amounts by the urine after full doses of chloral, camphor, and other similar substances. As it responds to the copper and other reduction tests like glucose, it is the source of a fallacy in testing the urine for that substance. Glycuronic acid does not ferment with yeast nor form glucosazone with phenylhydrazin acetate. The free acid is dextro-rotatory, but its usual compounds, the conjugate glycuronates, are levo-rotatory.

Levulose ($C_6H_{12}O_6$) (*Fructose, Fruit-sugar*).—This is the portion of the sweet juices of fruits and of honey which does not

crystallize; or does so with great difficulty. It is the sole product of hydrolyzing by acids the *Inulin* of artichokes, which resists the digestive ferments. In composition it is a *ketose*, its constitutional formula being $CH_2OH(CHOH)_3CO \cdot CH_2OH$. It is obtained, with an equal quantity of dextrose, when cane-sugar is *inverted* by hydrolysis with dilute mineral acids:

$$\underset{\text{Cane-sugar.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Levulose.}}{C_6H_{12}O_6}$$

Its name is derived from its levorotatory property, turning the polarized ray strongly to the left, as shown by its equation, $[\alpha]_D = -93°$ (p. 61). As this is a greater angle than that of dextrose, *inverted sugar* is slightly levorotatory. An explanation of the optical difference is found in the stereochemical formulas of dextrose and levulose. Dextrose is the aldehyd of the alcohol sorbite, or $CH_2OH(CHOH)_4COH$. Levulose is the ketone of the alcohol mannite or $CH_2OH(CHOH)_3CO \cdot CH_2OH$ which shows it to have the ketone group CO and in addition alcohol groups at both ends. By oxidation it readily yields acids and ultimately oxalic acid. Like dextrose, it reduces Fehling's solution, by virtue of two alcohol groups, and forms glucosazone with phenylhydrazin. It is less fermentable than dextrose.

Seliwanoff's Test.—The reagent is made by dissolving 0.05 gm. of resorcin in 100 c.c. of dilute (1 : 2) hydrochloric acid. To get reliable results, the details must be sacredly carried out as follows: Into a test-tube put 5 c.c. of the reagent, add a few drops of a solution of levulose and heat quickly to the boiling-point, but do not continue boiling. Levulose causes a red color followed by a red precipitate, which when separated dissolves in alcohol bright red. Note that prolonged boiling with hydrochloric acid may change dextrose into levulose.

Both dextrose and levulose have been made by synthesis from formaldehyd. By adding milk of lime to an aqueous solution of formaldehyd *formose* is obtained. Formose is a mixture of different sugars of the formula $C_6H_{12}O_6$, apparently polymerized formaldehyd:

$$\underset{\text{Formaldehyd.}}{6CH_2O} = \underset{\text{Glucose.}}{C_6H_{12}O_6}$$

The mixture can be made to yield both dextrose and levulose.

Galactose, $C_6H_{12}O_6$ or $CH_2OH(CHOH)_4COH$, is formed by the hydrolysis of milk-sugar, and also by boiling certain gums with dilute sulphuric acid. It crystallizes in prisms, reduces copper solutions, is strongly dextrorotatory, and ferments with yeast. Oxidized with nitric acid, it yields mucic acid.

Inosite ($C_6H_{12}O_6$) (*muscle-sugar*) occurs in beans and peas, the liquid of muscular tissue, and in various organs of the body. Traces are found in normal urine, the amount increasing in diabetes and in some cases of Bright's disease. Although mentioned in this place among the carbohydrates because of its sweet taste, its true composition is *hexahydroxy-benzol*, $C_6H_6(HO)_6$. It does not reduce Fehling's solution nor ferment with yeast, but undergoes the lactic and butyric fermentations.

The Pentoses ($C_5H_{10}O_5$).—All the pentoses yet studied are aldoses with the constitutional formula $CH_2OH(CHOH)_3COH$. *Arabinose* is a product of the action of dilute sulphuric acid on cherry gum; *xylose* (*wood-sugar*) is obtained in the same way from wood, gum, and straw. Other polysaccharids than gum, such as the pentosanes of pears, are hydrolyzed by acids or by digestion in the body into pentoses. They are distinguished from ordinary sugars by the large amount of furfuraldehyd yielded when they are distilled with hydrochloric acid. The human urine, after ingestion of certain foods containing pentosanes, prunes, cherries, grapes, and beer, and also in certain persons as an anomaly in their metabolism, contains pentose, and this may constitute a fallacy in testing for glucose in supposed diabetics. Pentoses respond to Fehling's test, form osazones with phenylhydrazin, but are *not fermentable with yeast.* They develop a green color when heated with a saturated solution of orcin in hydrochloric acid (p. 625).

DISACCHARIDS

The empiric formula for this group in general is $C_{12}H_{22}O_{11}$. They appear to contain 2 molecules of monosaccharids, less the constituents of water, for by hydrolysis with dilute mineral acids they may all be resolved into 2 hexose molecules. Thus:

$$C_{12}H_{22}O_{11} \quad + \quad H_2O \quad = \quad 2C_6H_{12}O_6.$$

Taking up H_2O, cane-sugar *sucrose* becomes the hexoses, dextrose, and levulose; milk-sugar *lactose* is converted into dextrose and galactose; malt sugar *maltose* into 2 molecules of dextrose. A convenient division is made between those which do not reduce Fehling's solution (cane-sugar) and those which, like the hexoses, possess this power (lactose and maltose).

Cane-sugar, *saccharum*, U. S. P. ($C_{12}H_{22}O_{11}$) (*saccharose, sucrose*), exists widely distributed in the sugar-cane, sorghum, beet root, sugar maple, and in smaller amounts in pineapples, sweet berries, and other fruits. The expressed juice is freed from vegetable albumin, decolorized, evaporated until it begins to deposit crystals, and then in a centrifuge the crystals of sugar are

separated from the mother-liquor. The brown mother-liquor, called *molasses* or *treacle*, contains 50 per cent. of sugar that does not crystallize until various impurities are removed.

The crystals are hard four-sided prisms, soluble in one-third their weight of water, but slightly in alcohol. *Rock candy* is cane-sugar crystallized slowly and without agitation from concentrated solutions. *Beet-sugar* differs from cane-sugar only in being lighter in equal volumes. Cane-sugar melts at 160° C. (320° F.), and on cooling the liquid solidifies to a yellow, glassy, amorphous mass called *barley-sugar*. Heated to a higher temperature, it is decomposed into glucose and levulose. At 200° C. (392° F.) it loses water, and is converted into a brown mass called *caramel* or *burnt sugar*, used to color liquors and soups. Cane-sugar carbonizes when treated with warm concentrated sulphuric acid, in this respect differing from glucose.

The action of its aqueous solutions upon polarized light is the basis of a method of determining the degree of concentration. The polarizer used for this purpose is called a *saccharimeter*, and shows the deflection to the right, according to the formula $[\alpha]_D = +66.5°$ (p. 61).

After being hydrolyzed by boiling with acids the levulose product twists the ray in the reverse direction and the *invert-sugar* becomes levorotatory to a slight degree.

Cane-sugar is the only sugar that has no action on Fehling's solution, though it reduces potassium permanganate. Yeast does not excite alcoholic fermentation in it directly, but after some time a secondary ferment of the yeast, *invertase* or sucrase, develops from it dextrose and levulose, and these are fermentable. With phenylhydrazin it does not yield an osazone, differing in this respect from all the other sugars. These characteristic reactions are explained by the supposition that sucrose has no true aldose sugar group—CHOH . CO . H—but is composed of a dextroglucose and a levoglucose group, both in the glucosidic state united by their carboxyls (p. 440):

CH_2OH . CHOH . CH . CHOH . CHOH . CH
O
*Dextro*glucose residue. O

CH_2OH . C . CHOH . CHOH . CH . CH_2OH
O
*Levo*glucose residue.

With the hydroxids of strontium, calcium, and barium it combines to form soluble compounds called *saccharosates* or *sucrates*. The compound with calcium is used in medicine under the name of *syrupus calcis* (p. 238).

As it does not ferment readily, strong cane-syrups are used as preservatives of canned fruit. In the body an inverting enzym for cane-sugar occurs in the pancreatic and intestinal juices, which forms glucose more readily from maltose than from cane-sugar.

Maltose, $C_{12}H_{22}O_{11}$, with dextrin is produced from starch by the action of the ferment *diastase* in malted or germinated grain:

$$\underset{\text{Starch.}}{3(C_6H_{10}O_5)_n} + nH_2O = \underset{\text{Maltose.}}{nC_{12}H_{22}O_{11}} + \underset{\text{Dextrin.}}{nC_6H_{10}O_5}$$

$$\underset{\text{Maltose.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose.}}{2C_6H_{12}O_6}$$

This hydrolysis is accomplished to a limited extent by the action of dilute sulphuric acid upon cornstarch, as in the process for manufacturing commercial glucose. Ultimately it is completely converted into dextrose, showing that it is an anhydrid of that substance. It crystallizes with water in needles, is very soluble, is strongly dextrorotatory $[a]_D = +140.6°$, ferments readily with yeast, and reduces Fehling's solution. It forms an osazone with phenylhydrazin (Plate 3, *b*), which is soluble in boiling water. The constitution of maltosazone confirms the evidence of the other reactions, which indicate that of the two molecules of dextroglucose obtained by hydrolyzing maltose only one of the characteristic aldose sugar groups (CHOH . CO . H) preëxisted in the maltose. This justifies the following formula, in which molecule I forms a glucosid (p. 440) with molecule II, which alone has the true sugar group.

CH₂OH . CHOH . CH . CHOH . CHOH . CH
O
I. *dextro*glucose residue.
O
CH₂ . CHOH . CHOH . CHOH . CHOH . COH
II. *dextro*glucose residue.

Yeast contains, beside zymase and invertase, a third enzym *maltase*, which resolves maltose by hydrolysis into glucose.

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6.$$

If *maltase* is added to 20 per cent. maltose it changes only 86 per cent. to glucose; the equilibrium is reached with 14 per cent. of maltose left. This operation is reversed when the same enzym is added to 40 per cent. pure glucose. It builds up maltose until 14 per cent. is made, when the action balances (Fig. 30).

Milk-sugar, *saccharum lactis*, U. S. P. ($C_{12}H_{22}O_{11}$) (*lactose*), is found in the milk of mammalia in the average proportion of 4 per cent. After the removal of butter, fat, and casein in the manufacture of cheese, the remaining liquid yields, on evaporation, white and extremely hard crystals of lactose. Compared with cane-sugar it is less soluble and less sweet. While it reduces Fehling's solution, the process is much slower than when glucose is present. With phenylhydrazin it forms *lactosazone*, distinguished by its crystalline form (Plate 3 c.), but like maltosazone soluble in boiling water. It rotates the polarized ray to the right, $[a]_D = +52.53°$ (p. 61). With yeast of the ordinary variety it does not ferment. When the lactose of mare's milk is slowly changed into alcohol and lactic acid, *kumyss* is the product; *kephir* is the similar product obtained from cows' milk. By boiling with dilute acids milk-sugar is hydrolyzed and breaks up into dextrose and galactose:

$$\underset{\text{Lactose.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Galactose.}}{C_6H_{12}O_6}$$

The formula (p. 441) for the constitution of maltose will serve also for lactose, which is supposed to be a galactosid (glucosid) of glucose. *Test:* If 100 c.c. of a solution of either lactose or galactose be treated with 20 c.c. of concentrated nitric acid and evaporated on a water-bath to 20 c.c., the sugars are oxidized to mucic acid and a white precipitate forms in the clear liquid. No other sugars give this reaction.

TRISACCHARIDS

In the molasses of beet-sugar, in cotton and Australian manna, is *raffinose*, $C_{18}H_{32}O_{16}$, which is a carbohydrate dextrorotatory and partly fermentable by yeast. It resembles cane-sugar in chemical behavior, but has no true sugar group, as it yields no reaction to Fehling's solution or to phenylhydrazin. It hydrolyzes by boiling with acid:

$$\underset{\text{Raffinose.}}{C_{18}H_{32}O_{16}} + 2H_2O = \underset{d.\ \text{Glucose.}}{C_6H_{12}O_6} + \underset{l.\ \text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Galactose.}}{C_6H_{12}O_6}$$

POLYSACCHARIDS

These have the composition $(C_6H_{10}O_5)_n$, but the constitution has not been ascertained. When hydrolyzed by acids they betray a much higher complexity than the disaccharids, splitting into mono-saccharids, disaccharids, and dextrins. Thus, as stated on p. 441, starch is decomposed into maltose and dextrin, both of which have a very high molecular weight. The polysaccharids are colloids and

non-dialysable, both physical properties being generally associated with substances of a high molecular weight. If polysaccharids be regarded as aggregations of many molecules of the formula $(C_6H_{10}O_5)_n$, then disaccharids would be denoted by $(C_6H_{10}O_5)_2+H_2O$ and monosaccharids by $C_6H_{10}O_5+H_2O$.

Starch $(C_6H_{10}O_5)_n$ (*amylum*, U. S. P.) is found widely distributed in almost all the tissues of plants, but is most abundant in all kinds of grain and in nutritious tubers, such as the potato.

Fig. 80.—Potato starch (Wolf).

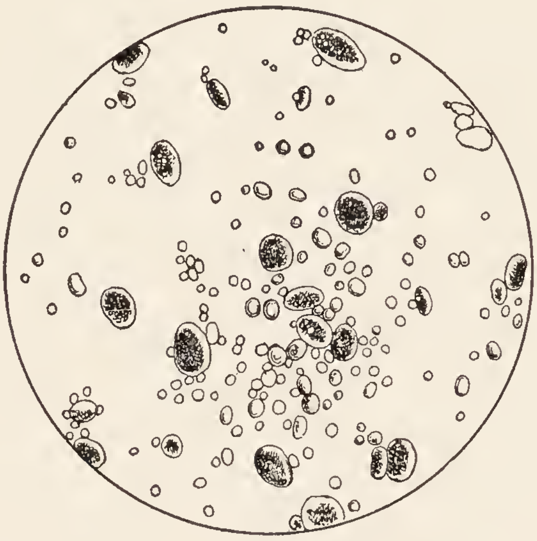


Fig. 81.—Wheat starch (Wolf).

The sugar and gluten are converted into soluble forms by rubbing and steeping in warm water, leaving starch to deposit from the washings as an amorphous mass. When dried it is a white powder, tasteless, odorless, and insoluble in cold water, alcohol, and ether. The microscope shows starch to be composed of granules marked with concentric striations and a cellulose envelope (Figs. 80 and 81).

The granules from different plants may be identified by their characteristic size, shape, and structure. When boiled in water these granules swell and burst, and a homogeneous white paste or jelly is formed. Prolonged boiling causes the *granulose* of the cell to pass into solution, leaving the cell wall or *cellulose* suspended.

Experiment 1.—Stir starch in cold water in a test-tube, filter, and test the filtrate with iodin. It does not turn blue because the starch has not dissolved.

Experiment 2.—Boil water in a test-tube and add a small quantity of cold starch and water. It forms a thin paste which, when cooled, turns blue with iodin (soluble starch or amylodextrin).

To assimilate the starch of food it must first be hydrolyzed by dilute acids or ferments into the monosaccharids, like glucose. The stages of conversion can be noted by the application of certain tests (Exps., p. 552).

The solution of starch (*amylodextrin*) yields a characteristic brilliant blue color with iodin, which disappears on heating to reappear on cooling. In the next stage (*maltodextrin* and *erythrodextrin*) iodin gives a red color. In the third stage (*achro-odextrin*) iodin gives no color. At last *maltose* and *dextrose* are formed and can be identified by Fehling's solution. In any sample of starch passing through these changes some portions of the intermediate products are present at all periods, as the process is continuous until complete.

A possible explanation of the progress of the transformation may be found in the hypothesis that the starch molecule has the great weight of $(C_{12}H_{20}O_{10})_{50}$. Breaking into 5 molecules of $(C_{12}H_{20}O_{10})_{10}$, it becomes soluble; hydrolyzed in successive stages it forms the series of dextrins and, simultaneously, maltose with each series. Cleavage is in the sense of this equation:

$$\underset{\text{Soluble starch.}}{(C_{12}H_{20}O_{10})_{10}} + 8(H_2O) = \underset{\text{Achroödextrin.}}{(C_{12}H_{20}O_{10})_2} + \underset{\text{Maltose.}}{8(C_{12}H_{22}O_{11})}$$

Dextrin $(C_6H_{10}O_5)_n$ (*British Gum*).—This is the general term applied to one or a mixture of isomeric substances obtained as transitional forms in the process of converting starch into dextrose. Besides the methods given above, it can be prepared by heating dry starch to 175° C. (347° F.).

In appearance and properties it resembles gum arabic. The commercial article is a yellowish amorphous powder, which in concentrated aqueous solution is mucilaginous and adhesive.

Gums (*arabin* and *bassorin*) are translucent amorphous substances found in many plants. In water the vegetable gums swell up and make mucilages. Boiled with dilute sulphuric acid they yield glucose.

Inulin $(C_6H_{10}O_5)_n$ is found in the food reserve of tubers of dahlia and artichoke and the roots of inula and other compositæ. It is a white, tasteless powder freely soluble in warm water. It is not colored by iodin, yet it hydrolyzes by acids and by *inulase* to a fructose, which reduces Fehling's solution. It is not affected by diastase nor the amylases of digestion and is, therefore, without food value.

Glycogen $(C_6H_{10}O_5)_{10}$ (*animal starch*) is a polysaccharid not found in plants, but largely in the liver and other tissues and cells of animals. It is partly derived from glucose by losing the elements of water, a dehydration reversed by enzyms in the muscles:

$$10C_6H_{12}O_6 \rightleftarrows (C_6H_{10}O_5)_{10} + 10H_2O.$$

Liver tissue minced and extracted with hot water yields it in an impure form. The albuminoid material may be precipitated by

acetic acid and potassium iodohydrargyrate, and the filtrate, treated with alcohol, deposits the pure glycogen. A white amorphous powder, without odor or taste; its aqueous solution rotates the polarized ray strongly to the right, $[a]_D = +196.6°$. With iodin it gives a wine red color which disappears o heating, to reappear on cooling. It does not reduce Fehling's solution, but is converted to glucose by dilute acids or certain enzyms. Like starch, it does not dialyze, but unlike starch it is readily soluble in cold water.

Cellulose $(C_6H_{10}O_5)_n$ (*Vegetable Fiber*).—In all plants the woody skeleton and cell membrane are composed mainly of this substance. It exists almost free from other matter in cotton-wool, linen, and hemp. Swedish filter paper is cellulose made pure y the bleaching and washing processes to which the raw fiber has been subjected. It is a complex polysaccharid, yielding, by hydrolytic cleavage, a disaccharid unlike the maltose produced from starch. Insoluble in water, alcohol, and ether, it dissolves in *Schweitzer's reagent* (ammoniacal solution of cupric oxid). From this solution it is deposited by acids as a gelatinous mass which changes by drying to a grayish powder.

Cellulose swells in and is slowly dissolved by concentrated sulphuric acid. This solution of wood fiber, diluted with water and boiled, yields dextrin and glucose. Though the cellulose itself is not digestible, it is thus transformable into valuable foods.

In the intestines of man cellulose of vegetable food is only to a limited extent dissolved: most of it passes out with the feces. In the herbivora only a small fraction reappears in the feces, showing that under the action of bacteria or enzyms it undergoes a fermentation into soluble products that are absorbed.

Nitric acid acting upon cellulose may form one of three nitrates as esters, showing that there are present in each original unit three hydroxyl groups indicated by the formula $C_6H_7O_2(OH)_3$. By dipping unsized paper for a few seconds in sulphuric acid the surface is changed to disulphate

$$C_6H_7O_2(OH)_3 + 2H_2SO_4 \rightleftarrows C_6H_7O_2(OH)(SO_4H)_2 + 2H_2O.$$

If this be washed in water the action is reversed, the acid is removed and the regenerated cellulose deposited in the pores. The paper is thereby greatly toughened like a membrane, and is substituted for *parchment* in documents and in dialyzers.

Guncotton (*Pyroxylin*).—Pure cotton wool treated with a mixture of nitric acid, 1 part, and sulphuric acid, 2 parts, washed and dried, is converted into *trinitrocellulose*, $C_6H_7O_2(NO_3)_3$. This is the violently explosive guncotton, insoluble in a mixture of ether and alcohol. If the cotton be dipped for a few minutes only, less

of the nitric group unites with it, the product being *mono-* and *di-*nitrates. These dissolve in a mixture of alcohol and ether with the formation of *collodion*, U. S. P., a colorless syrupy liquid. By the evaporation of the solvent the collodion is deposited as a transparent, smooth, contractile film, used as a surgical dressing or as a basis for photographic sensitive films.

Celluloid is pyroxylin mixed with camphor and coloring substances, and shaped by pressure. It is made non-inflammable by adding sodium or ammonium phosphate. *Elastic collodion* (*collodium flexile*, U. S. P.) contains castor oil and turpentine to render the collodium less contractile and constringent. It is used as a protective covering for wounds and abrasions. *Styptic collodion*, U. S. P., is flexile collodium made astringent by the addition of 20-per cent. tannic acid. *Cantharidal collodion*, U. S. P., has enough of the extract of cantharides to make it a blistering application.

Celloidin is a purified pyroxylin used to make dialyzers and for microscopic embedding.

Glucosids are natural principles of plants, which are hydrolyzed by alkalis, mineral acids, or certain enzyms, with the production of a sugar and a variable substance not a carbohydrate. The sugars formed are pentoses, hexoses, or disaccharids. The other product is usually a derivative of the benzene series with bactericidal properties. A large number of artificial glucosids have been prepared by the action of hydrochloric acid upon different sugars in the presence of alcohol. Thus, when a mixture of methyl alcohol and glucose is warmed with anhydrous HCl, there is first formed an additive compound, which eventually loses water, leaving methyl-glucosid:

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Methyl alc.}}{CH_3OH} = H_2O + \underset{\text{Methyl-glucosid.}}{C_6H_{11}O_5O \,.\, CH_3}$$

The plant glucosids are of like structure, being formed from a simple sugar and another molecule by elimination of water. The characteristic group is indicated in the general formula in which R stands for a radical, such as methyl:

$$\underbrace{CH \,.\, HCOH \,.\, HCOH \,.\, CH}_{O} \,.\, OR$$

The class includes amygdalin, convolvulin, digitalin, indican, helleborin, salicin, santonin, sinigrin, strophanthin, etc. *Amygdalin* ($C_{20}H_{27}NO_{11}$) occurs in bitter almonds, cherry, laurel, etc.; it is hydrolyzed by the enzym emulsin to dextrose, benzoic aldehyd, and hydrocyanic acid (p. 468). The significance of amygdalin in so many

plants is found in the bactericidal benzaldehyd and poisonous hydrocyanic acid liberated from it. As soon as moulds penetrate, or any injury breaks the integument of almonds and other seeds or the bark of the wild cherry, the histologic barrier between the glucosid and its enzym is broken down and the poisons set free to act as nature's antiseptic dressings. Every plant appears to have a protecting glucosid, like salicin in the willow, which yields saligenin or others aromatic compound having the antiseptic virtues of salicylic acid. In the bark of the pine family balsams have this function. *Myronic acid* or *sinigrin* occurs in black mustard as potassium myronate ($KC_{10}H_{18}NS_2O_{10}$) and is hydrolyzed by the ferment myrosin in cold water to dextrose, mustard oil, and acid potassium sulphate (p. 546). The acid sulphate in water dissociates sulphuric acid to act as antiseptic to the wounded seed.

Indican occurs in indigo-bearing plants. Hydrolyzed by enzyms in the leaf it forms indoxyl, thus:

$$\underset{\text{Indican.}}{C_{14}H_{17}O_6N} + H_2O = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Indoxyl.}}{C_8H_7ON}$$

Both indican and indoxyl are colorless, but the latter is oxidized by the plant enzym oxidase to the blue dye indigotin (p. 492). Urinary indican, though related to this glucosid, differs from it chemically (p. 595).

Phlorhizin is a glucosid in the bark of apple and pear trees which is hydrolyzed and split into dextrose and phloretin. When this drug is given it causes a transient glycosuria, with diminution of the normal amount of glucose in the blood. Its action is specific upon the kidneys; their soundness is tested by the degree of excretion of glucose after a dose of phlorhizin.

Carbohydrates in the Body.—Uncooked starch, being enclosed in an insoluble envelop, is not attacked by the enzyms of digestion in the saliva, but passes unchanged as far as the intestine, where part of it is decomposed by the bacteria and part digested. When its granules are burst by cooking the starch is set free and made partly soluble. The enzym of the saliva, salivary amalase and *maltase*, cause hydrolytic cleavage into soluble starch, dextrin, and finally maltose (p. 444). These changes go on in the mouth and even in the fundus of the stomach for a considerable time until gastric acidity is pronounced, when the portion yet undigested passes into the intestine to meet a rapid and powerful enzym, *amylopsin* of the pancreatic juice, also the amylases and invertases of the intestinal juices, which cause hydrolytic cleavage in the remainder of the starch, forming maltose, one molecule of which is split by an enzym in the epithelial cells of the stomach and intestines during transmission, to form two molecules of dextrose.

Cane-sugar is not altered by salivary amylase nor by pancreatic amylase, but before absorption is hydrolyzed to dextrose and levulose either in the stomach by the hydrochloric acid or in the intestines by the *sucrase*. The latter process is the more important. *Lactose* is hydrolyzed in the intestines by lactase, reaching the blood as dextrose and galactose.

Fermentations by yeast and bacteria occur in a variable portion of the dextrose before absorption. These are typified in the following equations:

1. $C_6H_{12}O_6 = 2CO_2 + 2C_2H_5OH$ (alcohol).
2. $C_2H_5 . OH + O_2 = H_2O + CH_3 . COOH$ (acetic acid).
3. $C_6H_{12}O_6 = 2C_3H_6O_3$ (lactic acid).
4. $2C_3H_6O_3 = 2CO_2 + 2H_2 + C_3H_7 . COOH$ (butyric acid).

As the dextrose in the portal vein passes through the liver, part of it is dehydrated to glycogen and is stored up; a large proportion passes the liver and is distributed throughout the body.

In the muscles part is dehydrated and stored as glycogen and part is oxidized to lactic acid or to carbon dioxid and water, to give energy. Part of it is converted and stored as fat. It is probable that the carbohydrate excess stored in the liver as glycogen is rehydrated to glucose as it is needed by the body at large.

Any excess of glucose in the blood over its normal amount, 0.1 to 0.2 per cent., is excreted at once by the kidneys, causing *glycosuria*. The kidneys do not form the sugar, but simply remove it. Among the cleavage products of protein metabolism are the sugars. One theory of the cause of glycosuria is based upon the fact that the pancreas and the ductless glands—adrenal, thyroid, and pituitary—have an influence on carbohydrate metabolism. The normal adrenals set free or "mobilize" the carbohydrates from the liver and other tissues by a secretion called an accelerator *hormone*. The normal pancreas regulates this metabolism by the retarding *hormone* of its internal secretion. When by disease the adrenals are stimulated to overproduction of the accelerator, or on the other hand the pancreatic retarder is lessened, an excess of the glycogen is mobilized and the abnormal amount of sugar in the blood is then separated by the kidneys.

CYCLIC COMPOUNDS

THE BENZENE OR AROMATIC SERIES

In the foregoing pages consideration has been given to the aliphatic compounds—that is, those of the paraffins, or the fatty series, and especially the derivatives of methane, CH_4, as the first of two main divisions of organic substances. The other division is known as the cyclic compounds or those of the *aromatic series*, or the derivatives of benzene, C_6H_6. Many of the compounds belonging to the fatty series can be prepared directly from petroleum, or derived by synthesis from it; and so most of the aromatic compounds are obtained from coal-tar by fractional distillation and laboratory processes.

As benzene is the lowest member, the whole group is called the *benzene series*, just as the other group is called the *methane series*. Certain compounds found in nature, such as benzoic acid, emit peculiar odors, which are sometimes agreeable. Chemical studies having shown that these can be derived from benzene, which is itself aromatic, the term has been applied to the whole group.

Coal-tar.—In the manufacture of *coal-gas* the *coal* is heated in closed retorts, the gas and other volatile products distilling out through a pipe, leaving solid *coke* behind. When the hot coal-gas is cooled, *tar* is one of the condensed substances, the coal-gas itself, after various washings, being collected in gasometers, from which it is distributed for lighting and heating purposes. The *coal-tar* is a thick black liquid, at one time treated as a refuse material. Modern chemistry has extracted from it a large number of organic compounds of the greatest medical and commercial value. The complex mixture of more than forty substances in the tar is subjected to fractional distillation at four temperatures, with the result that it is roughly separated into five fractions. By refining processes, (1) *light oil*, collected up to 170° C. (338° F.), yields the hydrocarbons *benzene*, *toluene*, and *xylene; pyridin* and other bases; *carbolic acid* or *phenols*. The (2) *carbolic oil*, collected between 170° C. and 230° C. (446° F.), consists principally of *carbolic acid* and *naphthalene*. That (3) collected between 230° C. (446° F.) and 270° C. (518° F.), is used, under the name *creosote oil*, in treating wood for preservation. It contains *cresol*, *carbolic acid*, *naphthalene*, and *anthracene*. (4) *Green oil*, coming off above 270° C. (518° F.), contains *anthracene* and certain hydrocarbons solid at common temperature. The residue in

the still (5) is *pitch*, employed hot as a varnish to protect wood and metal work.

All of these bodies contain at least 6 atoms of carbon, and the more complex aromatic compounds break up into simpler ones which contain at least 6 atoms. Through many changes the aromatic bodies retain the group of 6 carbon atoms, apparently joined to one another in such a way as to use up 18 of their combining powers, leaving 6 free. Of this class the simplest and most important illustration is *benzene*, C_6H_6. From it all the compounds of this class may be derived by substituting for 1 or more of the 6 hydrogen atoms those of other elements or more complex groups. These substances may be made in numerous cases to yield benzene when they are decomposed. In *light oil*, the first crude fraction distilled from coal-tar, are found 4 hydrocarbons, homologous with benzene; they are *benzene*, *toluene*, *xylene*, and *cumene*. From these, by synthetic process, the higher members and compounds are built up. In the following table they are arranged in the order of their molecular weight, according to the general formula, C_nH_{2n-6}.

BENZENE HYDROCARBONS

Benzene or Benzol,	C_6H_6.		
Toluene or Toluol,	C_7H_8,	or Methyl-benzene	$C_6H_5CH_3$.
Xylene or Xylol,	C_8H_{10},	or Dimethyl-benzene	$C_6H_4(CH_3)_2$.
Cumene or Cumol,	C_9H_{12},	or Trimethyl-benzene	$C_6H_3(CH_3)_3$;
		Tetramethyl-benzene	$C_6H_2(CH_3)_4$.

Benzene (C_6H_6).—Having removed carbolic acid from the *light oil* of coal-tar by agitation with soda, and the bases by sulphuric acid, distillation yields 90 *per cent. benzol*. By further fractional distillation and crystallization of the benzene in a freezing mixture, the commercial article is prepared.

Pure benzene in small quantities is prepared by heating pure benzoic acid with soda-lime:

$$\underset{\text{Benzoic acid.}}{C_6H_5 . COOH} = C_6H_6 + CO_2.$$

Properties.—At common temperatures benzene is a colorless, mobile, volatile liquid of specific gravity of 0.880, boiling at 80.5° C. (176.9° F.). Cooled to 5.4° C. (41.7° F.) it crystallizes. It mixes with petroleum, alcohol, and ether, but not with water. It has an ethereal, pleasant smell; is highly inflammable, burning

with the luminous, sooty flame indicative of richness in carbon. It is a ready solvent for iodin, fats, oils, and resins. Its chief use is in the manufacture of its derivatives, which are of great commercial importance.

Toxicology.—A narcotic effect is produced by the accidental inhalation of benzene vapor in factories. One ounce (30 c.c.) taken by the stomach caused death after symptoms such as headache, giddiness, bluish flush of the face, delirium, convulsions, and coma.

Constitution of Benzene.—Benzene behaves so differently from other hydrocarbons we have studied that its structure must be regarded as peculiar. Like the paraffins, it is extremely stable, decomposing with difficulty into simple compounds. Boiling alkalis do not affect it, and only very slowly is it oxidized by hot chromic acid. Chlorin and bromin at ordinary temperatures gradually attack the benzene molecule, forming by substitution chlorbenzene, C_6H_5Cl; brombenzene, C_6H_5Br; dichlorbenzene, $C_6H_4Cl_2$; dibrombenzene, $C_6H_4Br_2$, etc. While nitric acid does not act on the paraffins, with benzene it forms nitrobenzene by substitution of the nitro radical, $-NO_2$, for an atom of hydrogen:

$$\underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Nitric acid.}}{HO.NO_2} = \underset{\text{Nitrobenzene.}}{C_6H_5NO_2} + \underset{\text{Water.}}{HO.H}$$

These substitutions are indications that C_6H_6 is a *saturated* compound. It is not as fully saturated as methane, for in direct sunlight it forms with bromin *additive* compounds as high as hexabromid, $C_6H_6Br_6$, but never with more than 6 atoms. When studied very closely by elaborate experiments, it is evident that all the hydrogen atoms are alike in their relation to the carbon in the compound. Many facts combine to establish the following conclusions as their most reasonable explanation:

1. *The benzene molecule is symmetric.*

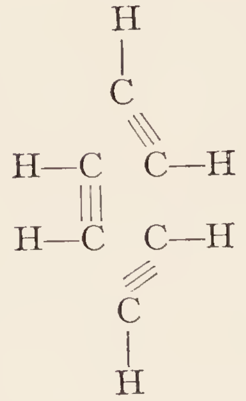
2. *The 6 carbon atoms form a closed chain or hexagonal ring, called the benzene nucleus.*

3. *Each carbon atom is directly united with only* 1 *atom of hydrogen.*

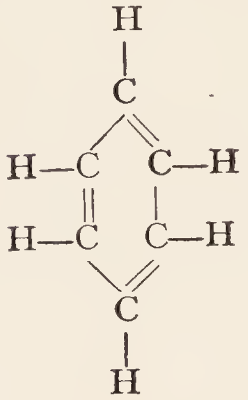
The *synthetic* method of preparing benzene is by heating acetylene without air, when 3 molecules are converted into 1 molecule of benzene by polymerization:

$$\underset{\text{Acetylene.}}{3C_2H_2} = \underset{\text{Benzene.}}{C_6H_6}$$

If we place the three molecules of C_2H_2 side by side, thus:

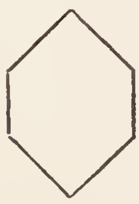


and suppose that each C atom turns a valence to its neighbor C atom, then the resulting molecule would be figured thus:

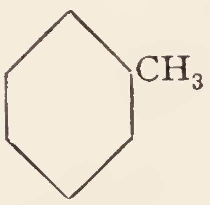


This graphic formula is used as a basis to represent all other facts ascertained concerning benzene and its derivatives, which are called *cyclic* because of this ring. When the ring contains 6 carbon atoms it is called *isocyclic;* if less than 6 carbon atoms, then it is called *heterocyclic.*

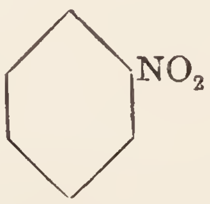
The entire theory of the constitution of organic compounds is based on the tetravalence of carbon. The above hexagonal ring shows 4 lines drawn from each carbon atom, 2 of the 4 lines meeting 2 other lines from the next carbon atom. Thus the carbon atoms are linked by 1 or 2 valences alternately. The ability to form *additive* compounds is accounted for by the fact that each carbon atom has 1 affinity not actively engaged. By substitution or addition to this ring as a basis an infinite variety of molecules are constructed. For convenience in description the figure of a regular hexagon without letters is used to represent the entire benzene ring. Used alone, it stands for the whole molecule C_6H_6; when other atoms or groups are written at the angles they are understood as being *substituted* for an atom of hydrogen. Thus:



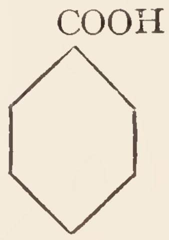
Benzene.
C_6H_6



Toluene.
$C_6H_5(CH_3)$



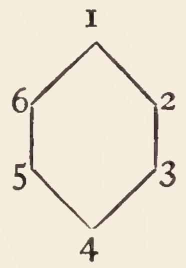
Nitrobenzene.
$C_6H_5(NO_2)$



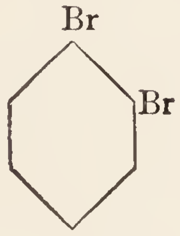
Benzoic acid.
$C_6H_5(COOH)$

But One Monosubstitution Product.—With any monovalent element, such as bromin, or group, such as $-NO_2$, there is formed by substitution but 1 monobenzene derivative. Thus, there is but 1 brombenzene, C_6H_5Br; 1 nitrobenzene, $C_6H_5 . NO_2$; 1 benzoic acid, C_6H_5COOH, etc. The only possible conclusion is that the hydrogen atoms of C_6H_6 do not differ in value.

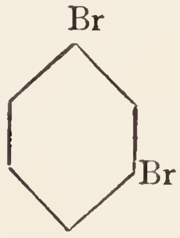
Three Isomeric Bisubstitution Products.—With derivatives of benzene containing 2, 3, or 4 substituted monovalent elements or groups, there are 3 isomeric compounds, corresponding to the three possible differences in the relative positions of the radicals or groups. For example, there are 3 different dibrombenzenes, $C_6H_4Br_2$; 3 dinitrobenzenes, $C_6H_4(NO_2)_2$, etc. For the difference in properties of the 3 isomers there is but one explanation, and that is based upon the fact that any hydrogen atom in the graphic benzene formula is placed symmetrically in relation to 2 pairs of hydrogen atoms, so that only three different substitution groupings are possible. If the carbon atoms of the hexagon are numbered as the hours on a dial, as shown below, omitting C and H,



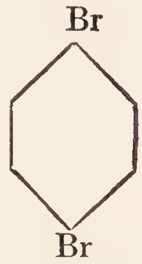
then with monovalent bromin it is possible to have only the three different positions for 2 substituted atoms, as shown below:



1 : 2 Adjacent: ortho-position.



1 : 3 Unsymmetric: meta-position.

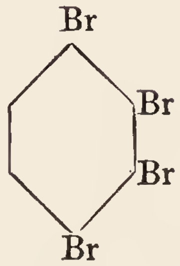


1 : 4 Symmetric: para-position.

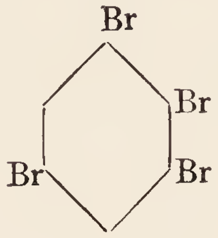
Where the 2 replacing atoms or groups occupy *adjacent* or *consecutive* positions, they form *ortho*-compounds (*orthos* = straight), abbreviated as *o*- or 1 : 2. When the arrangement is *unsymmetric*, it is called a *meta*-compound (*meta* = after), abbreviated *m*- or 1 : 3. If *symmetric* in position, the product is a *para*-compound (*para* = beside), abbreviated *p*- or 1 : 4.

When 3 or 4 atoms of hydrogen are displaced by as many identical atoms or groups, 3 isomers result, and can be accounted for if their constitutions are as represented in the following for-

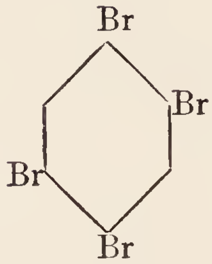
mulas for the 3 tetrabrombenzenes, using the simple unnumbered hexagon:



1 : 2 : 3 : 4 Adjacent: ortho.



1 : 2 : 3 : 5 Unsymmetric: meta.



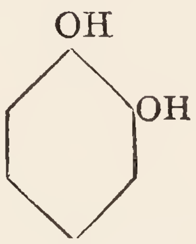
1 : 2 : 4 : 5 Symmetric: para.

When the simple hexagon without letters is used instead of the formula C_6H_6, the conversion into a molecular formula is made by writing C_6 for the hexagon, allowing 1 hydrogen atom for each unoccupied corner, and writing the substituting atoms or radicals last. Thus:

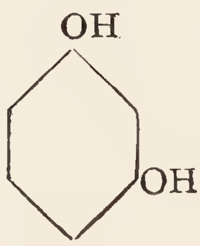
The three molecular formulas for the tetrabrombenzene, the graphic formulas of which have just been given, would be written $C_6H_2Br_4$. To distinguish each of the three it is customary to precede the formula, or to append in parenthesis below the line the numbers indicating the angles taken by the replacing element:

Ortho-$C_6H_2Br_{4(1, 2, 3, 4)}$; meta-$C_6H_2Br_{4(1, 2, 3, 5)}$;
para-$C_6H_2Br_{4(1, 2, 4, 5)}$. Or they may be written
ortho-1 : 2 : 3 : 4 – $C_6H_2Br_4$; meta-1 : 2 : 3 5-$C_6H_2Br_4$;
para-1 : 2 : 4 : 5 – $C_6H_2Br_4$.

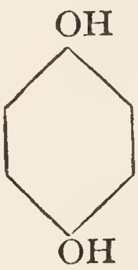
Another illustration is seen in the three different substances in which hydroxyl groups have been substituted for 2 hydrogen atoms. Careful research has established the fact that their constitutional formula should be written:



Ortho-



Meta-



Para-

The one molecular formula for all three is $C_6H_6O_2$, but this does not indicate their true structure, as *dihydroxybenzenes*. A complete conversion of the graphic hexagons is made as follows, the common name being given after each formula:

o-dihydroxybenzene = $C_6H_4(OH)_{2,(1-2)}$ or *pyrocatechol.*

m-dihydroxybenzene = $C_6H_4(OH)_{2(1-3)}$, or *resorcinol.*

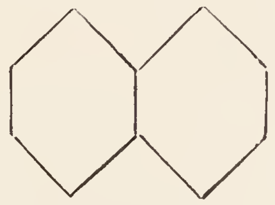
p-dihydroxybenzene = $C_6H_4(OH)_{2(1-4)}$, or *hydroquinol.*

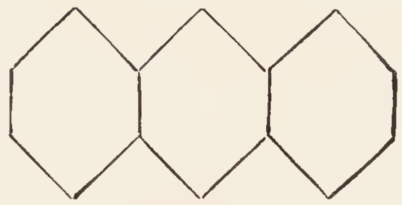
General Properties of Aromatic Compounds.—The members of the benzene series, like those of the methane division, form halogen derivatives, and also alcohols, aldehyds, ketones, acids, nitro- and amido-compounds. Reference has already been made to their characteristic behavior and ready reaction with nitric acid. When the aromatic nitro-compounds are reduced, *amido*-compounds are produced, containing the amido-group, $-NH_2$. Thus:

$$\underset{\text{Nitrobenzene.}}{C_6H_5 . NO_2} + 6H = \underset{\text{Amidobenzene or anilin.}}{C_6H_5 . NH_2} + 2H_2O.$$

When the amido-compounds are treated with nitrous acid in the cold, the products are *diazo*-compounds and not alcohols, as would be the case if fatty amins were so treated. The diazo-compounds are unstable bodies in which the hydrocarbon radical is joined to a double atom of nitrogen, having one free affinity. Thus: diazobenzene is $C_6H_5 . N_2 . OH$.

Among the indirect derivatives of benzene are substances like *diphenyl*, $C_6H_5 - C_6H_5$, which is regarded as formed by the union of two *phenyl* groups, resembling in this respect ethane or dimethyl, $CH_3 - CH_3$. To explain the structure of some other hydrocarbons it must be assumed that combination occurs between 2 or more closed chains or nuclei which have 2 or more carbon atoms in common. These substances are considered (p. 475) as *polynucleated* compounds, *i. e.*, containing more than one benzene nucleus.


Naphthalene.

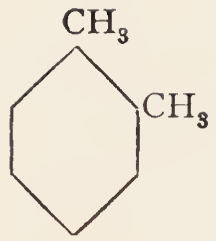

Anthracene.

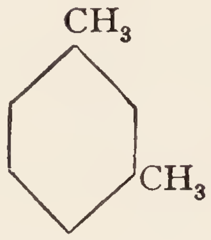
Toluene ($C_6H_5 . CH_3$) (*toluol, methyl benzene*) is so named because it can be obtained by dry distillation of balsam of Tolu and other resins, though it is always manufactured from coal-tar.

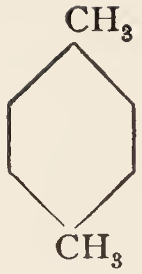
It is a mobile liquid, pleasant smelling and inflammable, does not mix with water, resembling benzene, but having some properties that are different, due to the methyl group in its composition. When oxidized the CH_3 of the methyl is changed to the acid group $-COOH$ and water, but the benzene ring is unaltered.

$$\underset{\text{Methyl benzene.}}{C_6H_5 . CH_3} + 3O = \underset{\text{Benzoic acid.}}{C_6H_5 . COOH} + H_2O.$$

Xylene ($C_6H_4(CH_3)_2$) (*xylol, dimethylbenzene*) exists in the three isomeric forms, given below:


Orthoxylene.


Metaxylene.


Paraxylene.

These three varieties exist in coal-tar and in commercial xylol, and can be prepared synthetically from toluene. They are much alike in physical properties, being liquids, ethereal, of pleasant odor, and inflammable. In chemical properties there are certain marked differences.

Cumene ($C_6H_3(CH_3)_3$) (*trimethylbenzene*) is usually obtained from coal-tar. It is the third of the homologues of benzene.

Cymene ($C_{10}H_{14}$ or $C_6H_4 . CH_3 . C_3H_7$) (*paramethyl-propylbenzene*) is an important pleasant-smelling hydrocarbon occurring in the ethereal essences of thyme and many other plants. It is easily prepared from camphor with phosphorus pentoxid:

$$\underset{\text{Camphor.}}{C_{10}H_{16}O} \quad = \quad \underset{\text{Cymene.}}{C_{10}H_{14}} \quad + \quad H_2O.$$

Its relation to turpentine is shown by the ease with which it is produced when that substance is oxidized by being heated with iodin:

$$\underset{\text{Turpentine.}}{C_{10}H_{16}} \quad + \quad O \quad = \quad \underset{\text{Cymene.}}{C_{10}H_{14}} \quad + \quad H_2O.$$

Terpenes.—The hydrocarbon *terebenthene*, $C_{10}H_{16}$, constituting pure oil of turpentine, *terebinthina*, U. S. P., is classed with its numerous isomers as terpenes. They may be regarded as derived from cymene by the addition of 2 atoms of hydrogen. They resemble turpentine chemically and physically, and are the essential constituents of many volatile oils, such as lemon, juniper, bergamot, rosemary, and other *essences*. They are polymerized when mixed with strong sulphuric acid; are converted to cymene by the halogens; and oxidized to several acids by nitric acid.

Turpentine not being water soluble is given internally suspended in *emulsum olei terebinthinæ*, U. S. P., which contains gum acacia, syrup, oil of almond, and water. Dose: 1 fl. dr. (4 c.c.). When oil of turpentine is treated with nitric acid and alcohol it is converted to *terpin* or turpentine camphor, a diatomic alcohol, $C_{10}H_{18}(OH)_2$. When united with water this forms *terpini hydras*, U. S. P., in the form of colorless crystals of bitterish taste, permanent and water soluble. *Dose*, as an expectorant: 3 to 10 gr. (0.2–0.6 gm.).

Terebene, U. S. P., is obtained by the action of sulphuric acid on oil of turpentine. It consists chiefly of pinene, $C_{10}H_{16}$. It is a yellowish liquid of thyme-like odor and aromatic taste, forming resin by exposure to light. It is sparingly soluble in water, freely so in alcohol and ether, and is used internally as an expectorant, externally as an antiseptic. *Dose:* 5 to 10 ♏ (0.3–0.6 gm.).

Stearoptens (*camphors*) are solid residues formed when turpentine and allied substances are distilled with steam. *Camphor*, U. S. P., a dextrogyrate ketone, $C_9H_{16}CO$, is a crystalline solid of characteristic odor, obtained from the camphor tree. *Artificial camphor*, $C_{10}H_{16}HCl$, is produced by the direct union of oil of turpentine and hydrochloric acid. *Menthol*, $C_{10}H_{20}O$, is a solid stearopten found in oil of peppermint. *Thymol*, U. S. P., $C_{10}H_{14}O$, is a solid cymylic phenol found in oil of thyme. It is crystalline, has a hot taste and aromatic odor. Very soluble in alcohol and ether, it is only sparingly so in water. It is used in various surgical preparations as an efficient and agreeable antiseptic. *Thymolis iodidum*, U. S. P., $C_{20}H_{24}O_2I_2$, *dithymol diodid*, *aristol*, is a red, amorphous powder made by action of solution of iodin in potassium iodid on alcoholic solution of thymol. It contains 45 per cent. iodin and is used as an aromatic substitute for iodoform in surgical dressings. It should be kept in amber-colored bottles. *Eucalyptol*, U. S. P., $C_{10}H_{18}O$, is a camphoraceous liquid found in oil of eucalyptus. It is insoluble in water, but soluble in alcohol and oils; used externally as an antiseptic, internally for lung diseases.

BENZENE HYDROXIDS (Phenols)

There are no fatty prototypes to the phenols. They contain the hydroxyl group substituted necessarily for an atom of hydrogen of the benzene nucleus itself. Thus, ordinary phenol is $C_6H_5 . OH$. Their constitution is different from that of a primary alcohol and hence when oxidized they do not yield an aldehyd, and, further on, an acid, nor form an ester with an acid, as does ethyl alcohol.

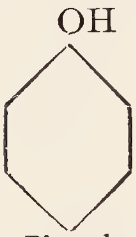
In the higher homologues of benzene, which contain hydrogen in a side chain, there are substances which contain the hydroxyl group and behave on oxidation like ethyl alcohol. These are called *aromatic alcohols* and are illustrated in benzyl alcohol, $C_6H_5 . CH_2OH$, derived from toluene, $C_6H_5 . CH_3$, by the substitution of $-OH$ for an H of $-CH_3$. These, when oxidized, form aromatic aldehyds, such as benzaldehyd, $C_6H_5 . COH$; and aromatic acids, such as benzoic acid, $C_6H_5 . COOH$.

The two kinds of aromatic hydroxy-compounds then are (*a*) *phenols* and (*b*) *aromatic alcohols*. As all 6 of the hydrogen atoms of the benzene nucleus may be replaced by hydroxyl, the

phenols may be monohydric, dihydric, trihydric, etc., according to the number of hydroxyl groups they contain.

Carbolic acid, $C_6H_5 . OH$, is a monohydric phenol, as is also cresol or hydroxytoluene, $C_6H_4(CH_3) . OH$. Resorcinol or dihydroxybenzene is a dihydric phenol, and phloroglucinol, $C_6H_3(OH)_3$, a trihydric phenol.

Carbolic acid ($C_6H_5 . OH$) (*phenol*, U. S. P., *hydroxybenzene*) occurs in traces in the urine, in the form of phenolsulphonate of potassium, $KC_6H_5SO_4$. This compound is derived from the protein of the body. The sole source of the commercial article is coal-tar. The *heavy oil* is treated with sodium hydroxid, which combines with the phenol and then, on the addition of sulphuric acid, precipitates in a crude state as an oil. By more complex methods it can be obtained from brombenzene, nitrobenzene, anilin, or salicylic acid.


Phenol.

It can be prepared from benzene indirectly by the following stages: Nitric acid ($HONO_2$) making nitrobenzene, which is reduced to amidobenzene by hydrogen: this by the action of nitrous acid (HONO) evolves free nitrogen, retaining hydroxyl.

$$\underset{\text{Benzene.}}{C_6H_6} \rightarrow \underset{\text{Nitrobenzene.}}{C_6H_5NO_2} \rightarrow \underset{\text{Amidobenzene.}}{C_6H_5 . NH_2} \rightarrow \underset{\text{Phenol.}}{C_6H_5 . OH}$$

Acidum Carbolicum Impurum.—To purify carbolic acid further treatment is necessary with lime and hydrochloric acid, accompanied with successive distillations. Crude phenol is brown red, more acid than the pure, and has a stronger odor, due to cresols.

Properties.—The volatilized product condenses in long colorless or faint red needles, having a characteristic odor, and when dissolved in much water a caustic, sweetish taste. It turns pink on exposure to light and deliquesces in moist air, but dissolves with difficulty in 15 parts of cold water, is readily soluble in boiling water, alcohol, ether, glycerin, chloroform, and the oils, but not in petroleum and benzin. The crystals melt at 43° C. (109.4° F.), and, agitated with 10 per cent. of water or glycerin, they become *phenol liquefactum*, containing 86.4 per cent. by weight of absolute phenol. This is the most convenient form for dispensing or for other uses. It is a protoplasmic poison, coagulating albumin, and hence fatal to all forms of life. This makes it a potent bactericide, used especially in surgery for destroying the germs that infect wounds. Its reaction is neutral or feebly acid; it leaves a greasy, reddish stain upon blue litmus paper. With strong bases it forms carbolates or phenolates, in accordance with this equation:

$$C_6H_5OH + NaHO = C_6H_5ONa + H_2O.$$

With alkaline sulphates it forms non-poisonous salts of phenolsulphonic acid, called phenolsulphonates:

$$\underset{\text{Phenol.}}{C_6H_5OH} + \underset{\text{Sodium sulphate.}}{Na_2SO_4} = \underset{\text{Sodium sulphophenolate.}}{NaC_6H_5SO_4} + NaHO.$$

Dose: $\frac{1}{2}$ to 2 gr. (0.03–0.13 gm.), well diluted. Among the official preparations are *glycerite* (1 part to 4 of glycerin); *ointment*, 3 per cent.

When the crystals are triturated with the following substances a liquid or soft solid product is obtained: camphor, chloral hydrate, acetanilid, lead acetate, menthol, phenacetin, resorcin, salol. It coagulates collodion.

Toxicology.—Owing to its common use as a disinfectant it can easily be bought by the suicide at any druggist's. Standing about the sick-room as an amber-colored oily liquid, it has been often mistaken for castor oil or alcoholic drinks. The death-rate from it places it in the list of suicidal poisons next to opium and its preparations and alkaloids.

Symptoms.—These may be considered under two heads: Those due to the local effects, and those that are systemic in character. Upon the mouth, esophagus, stomach, and intestines it acts as an energetic corrosive poison. When absorbed it quickly arrests normal action in the nervous system, and causes death by paralysis of the respiratory and cardiac centers.

If some of it touch the skin about the mouth, it causes burning, tingling, and numbness, followed by a white eschar. The corroded skin tissue separates in a few days and the white spot is succeeded by a brown stain. When it is swallowed the patient complains of a burning pain in the mouth, throat, and stomach, with or without retching and vomiting. There is distention of the abdomen and a strong odor of carbolic acid on the breath. The remote systemic effects are the same whether the point of absorption be the skin, the lungs, an open wound, the stomach, or other body cavities. The symptoms are muscular twitchings, weakness, pallor, nausea, clammy skin, headache, giddiness, delirium, thready and rapid pulse, irregular breathing. Lividity, coma, rarely convulsions, imperceptible pulse, and halting respiration usher in the final scene. In the meantime the urine is albuminous and bloody.

The greater part of the phenol changes by contact with the sulphates in the body to phenolsulphonates and the simple sulphates disappear from the urine. The normal ratio of the simple sulphates of the urine to the conjugate sulphates is as 10 : 1. A portion of the phenol is changed to phenol-glycuronic acid and is eliminated as harmless conjugate alkali salts. A considerable

portion is oxidized to the dihydroxybenzenes, pyrocatechol, and hydroquinol. These also form conjugate sulphates. In the urine they oxidize further to quinon ($C_6H_4O_2$), a dark greenish or black substance.

Fatal Dose.—Though 15 gr. (1 gm.) would cause dangerous symptoms when taken by the stomach, a fatal result is not likely unless 60 gr. (4 gm.) have been taken. Recovery has ensued after 1 fl. oz. (30 c.c.) has been swallowed. Absorbed from a wound, from the rectum or uterus, 15 gr. (1 gm.) would probably kill.

Fatal Period.—Large doses or external application to open cuts may destroy life in ten minutes. Usually death is not delayed beyond two hours, though there are cases where death has not occurred for several days.

Treatment.—The local anesthesia prevents the action of ordinary emetics. Oils are forbidden because they increase the diffusion of the poison. A liberal dose of whisky or alcohol is often given as a diluent. It should be followed by the introduction of the soft stomach-tube and washing with *syr. calcis*, or sodium sulphate one ounce in a glass of water until the contents of the stomach lose their peculiar odor. Sodium sulphate forms the relatively harmless sodium phenol-sulphonate. *Dependence should not be placed on alcohol as an antidote.*

If carbolic acid be applied to the skin, the mucous membrane, or open wound, and quickly followed by a lotion of alcohol, the corrosive action does not occur, and there are no constitutional symptoms. Some of this controlling action may be the effect of prompt dilution with a perfect solvent. It is not unlikely that alcohol, as a solvent, causes the molecule to dissociate in different ions from those that form in aqueous solution. If ferric chlorid be added to the solution in water, a violet-colored reaction appears; with the alcoholic solution it is brownish. If, however, water be added to the mixture with alcohol, the brownish liquid changes to violet. If the alcohol and carbolic acid be allowed to remain in the stomach, osmotic flow of water dilutes the alcohol, and in a few minutes absorption begins and the effects are those of a poisonous aqueous solution. To obviate this danger the lavage must remove the poison as soon as alcohol has been given. The antidotes of approved value are sodium sulphate, raw eggs, milk, and saccharate of lime.

For the coma and cardiac depression benefit may follow alternations of hot and cold affusions and the administration of hypodermic injections of atropin or strychnin. For failure of breathing resort should be had to artificial respiration. Prolonged rest in bed is necessary to prevent sudden collapse.

Postmortem Appearances.—The corroded spots about the lips, and the mucous lining of the mouth and esophagus are white and corrugated. The stomach mucous membrane is hardened,

white in patches, wrinkled, denuded in parts, showing the red inflamed structure beneath. Hemorrhagic points show where blood has been poured into the gastric contents.

Like changes appear in the duodenum. The characteristic odor of carbolic acid is discernible in the body, in the fluid of the ventricles of the brain, and in the urine. The urine is dark-greenish and shows little reaction to barium chlorid, the sulphates being conjugate with phenol.

Tests.—1. The odor is characteristic.

2. Carbolic acid coagulates albumin and also the clear collodion solution.

3. A trace of ferric chlorid gives an amethystine-blue color to aqueous solutions of carbolic acid. This test is interfered with by alcohol, ammonia, the mineral acids, and excess of ferric chlorid, all of which prevent the full development of the reaction. Creosote turns ferric chlorid brown and green.

4. Strong bromin water added to weak carbolated solutions precipitates white crystals of *tribromphenol.*

5. When boiled with *Millon's reagent*,[1] made fresh, solutions of carbolic acid turn red. If the change does not occur, it may require the addition of a few drops of nitric acid. The same reaction is produced by other phenols and the proteins, as is shown when pieces of dry albumin or dry bread are boiled in Millon's reagent; they turn dark red.

This reaction always denotes the OH group attached to the benzene ring (oxyphenyl). Given by the proteins it indicates in them the presence of this same combination existing in the cyclic compound *tyrosin* (p. 506).

6. A solution of carbolic acid is gently warmed with a small quantity of ammonia water and a few drops of solution of chlorinated lime. A blue color is produced, which changes to red on being acidulated. If the blue color fade, it may be restored by the addition of more of the chlorinated lime.

Detection.—A portion of the blood or the liver is digested for one hour with dilute sulphuric acid (2 per cent.). After straining, the liquid is mixed with dilute alcohol (1 to 3) and filtered. Having treated 30 c.c. of this with a few drops of ammonia, it is added to a reagent prepared as follows: To 20 c.c. of a solution of anilin containing 3 drops to 100 c.c. of water, add sodium hypochlorite sufficient to make a brown color. When the extract from the liver or blood is added to this reagent a permanent blue color indicates the presence of carbolic acid.

[1] A mixture of mercuric and mercurous nitrates containing some free nitrous acid, made by adding 5 c.c. of fuming nitric acid to 0.5 c.c. of mercury. The mercury must dissolve without boiling and the solution is then diluted with two volumes of water, and after several hours decanted. It does not keep long.

The urine is titrated with $BaCl_2$ to see if the simple sulphates are less than normal. It is then filtered from $BaSO_4$ and boiled with HCl to break up the phenolsulphonates. Tested again with $BaCl_2$, if a heavier precipitate falls, there is excess of phenolsulphonates, due to phenol (p. 604).

Phenolsulphonic acid ($C_6H_4(OH) . SO_3H$) (*sulphocarbolic acid*) is formed when phenol is dissolved in concentrated sulphuric acid (for Sulphonic Acids see p. 416):

$$C_6H_5OH + H_2SO_4 = C_6H_4(OH) . SO_3H + H_2O.$$

It is a syrupy liquid having a red color and feeble odor, and is freely soluble in water. It behaves as a monobasic acid, forming phenolsulphonate, of sodium, potassium, and other metals. The acid and its salts prevent fermentation, destroying low forms of animal and vegetable life, and are valued in medicine as antiseptics, being less irritating and poisonous than carbolic acid. The commercial *aseptol* or *sozolic acid* is a 30 per cent. solution of *o*-phenolsulphonic acid in water, used diluted to 10 per cent. as an antiseptic.

After the ingestion of phenol it is eliminated by the urine as a *potassium* phenolsulphonate ($KC_6H_5SO_4$), a conjugate or ethereal sulphate.

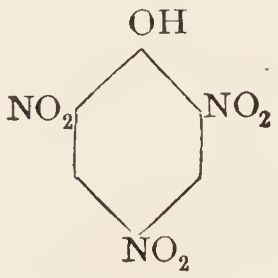
Sodii phenolsulphonas, U. S. P., $C_6H_4(OH)SO_3Na$, is a white crystalline salt, used locally as an antiseptic, and internally in fermentative dyspepsia. *Dose:* 10 to 30 gr. (0.6–2 gm.).

Zinci phenolsulphonas, U. S. P., $Zn(C_6H_5O_4S)_2 + 8H_2O$ occurs in colorless, tabular crystals used to make astringent solutions.

Ichthyol is the ammonium salt of a complex ichthyosulphonic acid having the formula $C_{28}H_{36}S_3O_6(NH_4)_2$. It is prepared from a mineral pitch found in the Tyrol, containing fossil fishes. It is a dark brown thick liquid with an unpleasant smell, soluble in water, oils, and glycerin. Applied locally, it is analgesic and antiphlogistic. It is *incompatible* with acids, alkalis, and alkaloids.

Trinitrophenol ($C_6H_2(NO_2)_3 . OH$) (*Picric Acid*).—When phenol is treated with dilute nitric acid it is converted into *ortho-* and *para*-nitrophenol, which separate as a dark brown oil or resinous mass. If this or a solution of phenol itself be gently heated with a few drops of nitric acid, 3 groups of NO_2 are taken up, the liquid turns yellow, and on cooling crystals of *picric acid* separate.

The constitution of trinitrophenol is represented by the formula:



It is the yellow substance formed by the action of concentrated nitric acid on woolen and silk fabrics, albumin, bread, and other nitrogenous animal matter, indigo, resins, leather, etc.

This *xanthoproteic* reaction always indicates the presence of the benzene ring, but not necessarily with the OH group attached, as in phenol. In the proteins are found not only *tyrosin*, but *phenylalanin*, both of which give this yellow color with nitric acid, due to trinitrophenol (picric acid). It is crystalline, odorless, intensely bitter, markedly acid, and slightly soluble in cold, but more easily so in hot water. It has the properties of a monobasic acid, readily decomposing carbonates and forming salts. Potassium picrate, $C_6H_2(NO_2)_3 . OK$, like the sodium and ammonium compounds, is a yellow crystalline substance, explosive under the action of heat or percussion. Picric acid itself burns quietly when ignited with caution, but under percussion or sudden heat explodes violently. It is used as a yellow dye for silk and wool. It is a valuable precipitant for albumin in Esbach's test, and for the alkaloids. Heated with glucose in alkaline solutions it produces a deep red color. Sometimes it is used as an adulterant for beer, because of its bitter taste and yellow color.

Toxicology.—Picric acid is sometimes applied to the skin in the treatment of skin diseases. The saturated aqueous solution forms an aseptic, protective scab when applied to burns. In strong alcoholic solution it irritates the skin, causing eczema; taken by the mouth the mucous membrane is irritated, by virtue of the necrosis due to the precipitation of the albumin in the tissues. There are vomiting of yellow matter, abdominal pain, and diarrhea with yellow stools. Without bile, the urine becomes red-brown owing to the presence of picraminic acid. The blood-corpuscles decompose and form methemoglobin. The eyes turn yellow and the skin itches, as in jaundice. Great weakness, stupor, and convulsions precede collapse.

Fatal Dose.—Poisoning has followed 30 gr. (2 gm.), but recovery has occurred after 90 gr. (6 gm.).

Treatment.—The stomach should be thoroughly washed out, and the bowels evacuated by enemata. The antidotes are proteins, as in raw eggs and milk. Glucose reduces the picric acid to a less injurious substance, and may be given freely.

Tests.—Having acidulated the material with sulphuric acid, ether is shaken with it to extract the picric acid. The residue after evaporation is dissolved in water, and a thread of cotton and one of wool placed in it. It is then acidified and warmed. The cotton is not dyed, but the wool stains yellow, yielding the color when immersed in alkaline solutions. When an alkaline solution of it is warmed with potassium cyanid a blood-red color is produced.

Cresol ($C_6H_4(CH_3) . OH$) (*Cresylic Acids, Hydroxytoluenes*).—The three next homologues of phenol are the *ortho-*, *meta-*, and

para-cresols, occurring in coal-tar and separable from it by fractional distillation. They resemble phenol as poisons of feeble solubility in water, in forming compounds with potassium and sodium, and in giving the bluish color with ferric chlorid.

Liquor cresolis compositus, U. S. P., is a solution of cresol in a soapy liquid made with linseed oil and potassium hydroxid. It is miscible with water in all proportions, and is a reliable and convenient disinfectant for the hands and instruments in the proportion of one part to twenty of warm water.

Creolin is a black syrupy antiseptic, containing a number of aromatic substances, chiefly cresols. It is less poisonous than carbolic acid. *Dose:* 5 to 15 min. (0.3–1 gm.).

Lysol is an oily liquid, saponified by boiling tar, oils, fat, and resin with alkali. It is an impure paracresol containing soap, soluble in water; antiseptic and less poisonous than carbolic acid.

Creosote is a complex mixture of phenol, cresol, guaiacol, $C_7H_8O_2$, creosol, $C_8H_{10}O_2$, phlorol, $C_8H_{10}O$, and other aromatic compounds produced by distillation of wood-tar. It is an oily liquid of peculiar odor and burning taste; colorless when fresh, but turning brownish on exposure to light. It is often adulterated with carbolic acid, which it resembles in being an antiseptic and a powerful irritant poison. It is used as a local application for toothache and a caustic for warts. It is to be distinguished from carbolic acid in its feebler solubility, in not crystallizing on cooling, in not coagulating the official collodium, and in giving with ferric chlorid a transient brownish, and not a bluish coloration.

Toxicology.—The poisonous effects are much like those of carbolic acid and guaiacol.

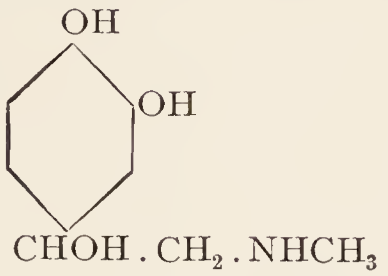
Dihydric Phenols ($C_6H_4(OH)_2$).—The three isomeric dihydroxybenzenes are well known and have much importance under the names pyrocatechol, resorcinol, and hydroquinol. Their respective formulas are given in another place (p. 454).

Pyrocatechol, *Catechol*, *o*-$C_6H_4(OH)_2$, is eliminated in traces by the human urine, having entered the circulation as a product of intestinal putrefaction. It also occurs in the drug catechu. It can be prepared by fusing phenolsulphonic acid with potash.

It is a colorless crystalline substance, soluble in water. In weak solution it can reduce Fehling's solution, and hence create a fallacy in testing for glucose in the urine. To detect it in the urine a considerable quantity of that fluid must be boiled with hydrochloric acid and then extracted with ether. The residue after evaporation is dissolved in water, and this solution gives with ferric chlorid a dark-green coloration which, on the addition of sodium bicarbonate, changes to violet and later to red.

This green color with ferric chlorid is given with all the dihydroxybenzenes. The preparation extracted from the supra-

renal gland, called *epinephrin* or *adrenalin*, yields the same reaction, showing the presence of catechol as a component. As methylamino-acetopyrocatechol it is made synthetically with this structure:



Guaiacol, U. S. P., $C_6H_4 . OH . OCH_3$, *methyl-pyrocatechol*, is a crystalline solid contained in the tar of beechwood, from which it is obtained by the fractional distillation of creosote. In *absolute guaiacol* it occurs as an oily liquid of aromatic odor, slightly soluble in water, freely so in alcohol and ether. It is used in medicine. *Dose:* 3 to 15 gr. (0.2–1.0 gm.). Its pharmaceutic compounds are the carbonate, benzoate, iodid, and salicylate.

Resorcinol ($C_6H_4(OH)_2$) (*resorcin*, *m-dihydroxybenzene*) is prepared by the action of fused potash on benzene-*m*-disulphonic acid. It can also be obtained by dry distillation of extract of Brazil wood, and by melting with caustic potash various resins, such as galbanum. Its structure has been referred to previously (p. 454).

It is a crystalline, colorless (turning red on exposure), sweetish substance, freely soluble in water, alcohol, and ether. It is odorless and antiseptic. Its aqueous solution turns a violet color with ferric chlorid. Under the name *Boas' reagent* (p. 557) an alcoholic solution of resorcinol and cane-sugar is used as a delicate test for free hydrochloric acid.

When the resorcinol is heated with phthalic anhydrid in a dry tube, a reddish mass is formed which, when dissolved in soda, gives a brownish solution. Added to water, this gives a beautiful red color with a yellow-green fluorescence. This shows the presence of *fluorescein* (resorcin-phthalein), $C_{20}H_{12}O_5$, an important dyestuff, from which is manufactured its sodium salt, *uranin*, $C_{20}H_{10}O_5Na_2$, another valuable dye. When fluorescein is treated with bromin, 4 atoms of hydrogen in the resorcin nuclei are displaced by bromin, forming *eosin*, a deep red dye with green fluorescence. Its potassium salt is a brownish powder which stains tissues a beautiful pink.

The medical effects of resorcin are those of phenol. It is used externally in skin diseases and in surgical dressings. By absorption from the skin it may cause the toxic nervous symptoms of phenol.

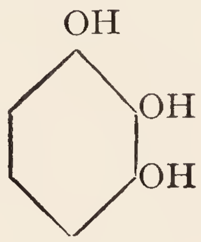
Dose of resorcin for seasickness: 2 gr. (0.13 gm.) every two hours; for antipyretic effects: 15 to 30 gr. (1–2 gm.). Its *incom-*

patibles are albumin, alkalis, antipyrin, acetanilid, exalgin, camphor, menthol, urethan, ferric chlorid, and spts. ætheris nitrosi.

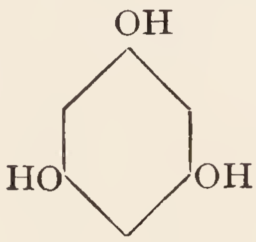
Hydroquinol ($C_6H_4(OH)_2$) (*quinol, p-dihydroxybenzene*) is a crystalline substance, readily soluble in water, and used in photography. It is an antipyretic in doses of 15 gr. (1 gm.).

Pyrocatechol, resorcinol, and hydroquinol are reducing agents, taking oxygen from other compounds and in the presence of alkalis even, from the air, turning to dark-green quinone ($C_6H_4O_2$). Hydroquinol is the most active in this respect.

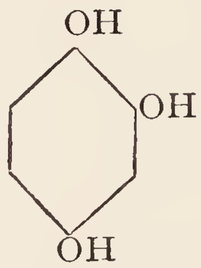
Trihydric Phenols ($C_6H_3(OH)_3$).—The three trihydric isomers possible in theory are all known; their constitutions are represented by the three formulas:



Pyrogallol.
1 : 2 : 3—Trihydroxybenzene.



Phloroglucinol.
1 : 3 : 5—Trihydroxybenzene.



Hydroxyhydroquinol.
1 : 2 : 4—Trihydroxybenzene.

Pyrogallol (*pyrogallic acid*) is prepared by heating gallic acid, at about 200° C. (392° F.), until CO_2 ceases to be evolved:

$$\underset{\text{Gallic acid.}}{C_6H_2(OH)_3 \cdot COOH} = \underset{\text{Pyrogallol.}}{C_6H_3(OH)_3} + CO_2.$$

It is a colorless crystalline substance readily soluble in water, and giving with ferric chlorid a red color. When ferrous sulphate is mixed with the ferric chlorid it yields a dark-blue color. Dissolved in alkalis, the solution turns black in the air from absorption of oxygen. By shaking this alkaline solution in a mixture of gases of known volume, the amount of shrinkage determines the oxygen present. In the presence of light and the salts of gold, silver, and mercury, it is oxidized to oxalic and acetic acids, while reducing the salts to the metallic state. Like hydroquinol, it is used as a developer in photography. It has been taken by mistake, with fatal results. Absorbed, it poisons the red corpuscles, causing them to shrink and lose their hemoglobin, which changes to methemoglobin, a brownish substance. This leads to jaundice and nephritis.

The symptoms are headache, chills, vomiting, cyanosis, dark urine, collapse, tremor, coma. The poison must be washed from the skin and the stomach. Stimulants and hypodermic injections of salt solution are called for.

Detection.—The material is shaken with ether to extract the pyrogallol. This is then tested with ferric chlorid and the silver

salts to show its reducing action. Millon's reagent gives a red color with it.

Phloroglucinol, 1 : 3 : 5 — $C_6H_3(OH)_3$, is obtained by fusing phenol with potash. It is colorless, crystalline, very soluble in water, and sweetish in taste. In making *Gunzburg's reagent* (p. 557) it is dissolved in alcohol with vanillin to detect free hydrochloric acid. A test for pentoses is made by warming with a mixture of phloroglucinol and hydrochloric acid; a deep red color develops.

Triketo-hydrindene-hydrate, marketed under the name **Ninhydrin,** has the formula:

$$C_6H_4{<}\begin{array}{c}CO\\CO\end{array}{>}C(OH)_2.$$

A crystalline synthetic product, it is soluble in water and alcohol and when heated reduces Fehling's solution. In neutral solution it gives a blue color with albumins, peptones, polypeptids, and α-amino-acids (with the exception of prolin, oxyprolin, and pyrrolidin-carbonic acid). The ninhydrin reagent is 0.1 gm. in 30 c.c. of distilled water. The test is as follows: To 1 c.c. of suspected liquid carefully neutralized, add 1 or 2 drops of the reagent and boil for one minute. As it cools the blue color is the positive indication. The test is interfered with if the reaction be either acid or alkaline.

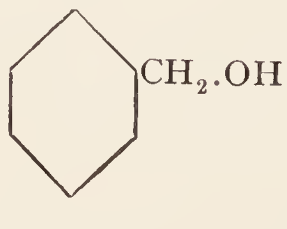
OXYGEN DERIVATIVES OF BENZENE

AROMATIC ALCOHOLS

When hydroxyl groups are substituted for the hydrogen atoms of the side chain in the aromatic hydrocarbons higher than benzene, substances are produced behaving like alcohols. Like the corresponding fatty alcohols, they are produced when the halogen derivatives are heated with water or weak alkalis, or by reducing the aldehyds. Thus, the simplest member:

$$\underset{\text{Benzyl aldehyd.}}{C_6H_5 . COH} \quad + \quad 2H \quad = \quad \underset{\text{Benzyl alcohol.}}{C_6H_5 . CH_2 . OH.}$$

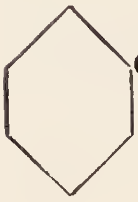
Benzyl Alcohol.—This compound contains the group: *carbinol,* $- CH_2 . OH$, and C_6H_5, or *phenyl,* and is therefore called *phenyl carbinol.* It occurs in the resins of styrax and balsams of Peru and Tolu. It is a colorless liquid, which oxidizes first into benzaldehyd and then into benzoic acid.



AROMATIC ALDEHYDS

These hold the same relationship to alcohols and acids as that existing between their analogues of the fatty series. They are the alcohols dehydrogenated.

Benzaldehyd (C_7H_6O or C_6H_5COH) (*Oil of Bitter Almond*).—This is obtained when the glucosid, *amygdalin*, and the ferment, *emulsin* (occurring in bitter almonds), are brought into the presence of water. As these are present in the kernels of cherries, peaches, and the bark and leaves of the cherry laurel, the same reaction results when these are macerated in water. The amygdalin is gradually decomposed into benzaldehyd, glucose, and hydrocyanic acid:


COH

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + 2H_2O = \underset{\text{Glucose.}}{2C_6H_{12}O_6} + \underset{\text{Hydrocyanic acid.}}{HCN} + \underset{\text{Benzaldehyd.}}{C_7H_6O}$$

By distillation, an oil (*oleum amygdalæ amaræ*) comes over which contains by weight 85 per cent. of benzaldehyd and 2 to 4 per cent. of hydrocyanic acid. In the laboratory benzaldehyd is prepared from benzal chlorid with dilute sulphuric acid.

It is a colorless liquid with the smell of almond and a burning taste, sparingly soluble in water, but freely in alcohol. In the crude oil of bitter almonds its association with hydrocyanic acid makes it poisonous (p. 194).

Vanillin.—*m-Methoxy-p-oxybenzaldehyd*, $C_6H_3.COH.(O.CH_3).OH$, is the odoriferous principle of vanilla occurring in colorless needles. The coniferous plants yield a glucosid, *coniferin*, which by oxidation gives vanillin. It is made by synthesis from guaiacol.

Salicylic Aldehyd.—*Salicylal*, *salicylous acid*, *o*-oxybenzaldehyd, $C_6H_4(OH)COH$, is the odoriferous principle in the essential oil of *Spiræa ulmaria*. It can be made by oxidizing salicin. It is an aromatic colorless oil having the properties of an aldehyd and a phenol.

AROMATIC ACIDS

The acids of the benzene series containing carboxyl, $-COOH$, are derived by substituting 1 or more such groups for the same number of hydrogen atoms. Substitution in the benzene nucleus itself yields, beside the simplest member, benzoic acid, $C_6H_5.COOH$, the 3 isomeric phthalic acids, dicarboxylic, $C_6H_4(COOH)_2$; the 3 tricarboxylic, $C_6H_3(COOH)_3$, etc. Toluene and the higher members having methyl side chains yield 2 classes of acids, according as the substitution is in the nucleus or in the side chain. Thus: there are 3 isomeric toluic acids, $C_6H_4 . CH_3 . COOH$, of

the first class, and phenyl acetic acid, $C_6H_5 . CH_2 . COOH$, of the second class.

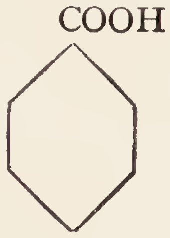
The only important aromatic carboxylic acid is benzoic. All aromatic hydrocarbons which contain only 1 side chain yield benzoic acid when oxidized with nitric or chromic acid. Thus:

$$\underset{\text{Toluene.}}{C_6H_5 . CH_3} + 3O = \underset{\text{Benzoic acid.}}{C_6H_5 . COOH} + H_2O.$$

When the hydrocarbons have 2 side chains, phthalic acid is formed.

The aromatic acids crystallize, are slightly soluble in water, and when heated usually volatilize without decomposing.

Benzoic acid, $C_7H_6O_2$, receives its name from its original source, *gum benzoin.* It is also present in balsam of Peru. As the compound hippuric acid or benzoylglycin it is present in the urine of herbivora. From the latter combination it can be obtained by boiling with hydrochloric acid:



$$\underset{\text{Hippuric acid.}}{C_6H_5 . CO . NH . CH_2COOH} + HCl + H_2O =$$
$$\underset{\text{Benzoic acid.}}{C_6H_5COOH} + \underset{\text{Glycin hydrochlorid.}}{NH_2 . CH_2 . COOH, HCl}$$

It can be sublimed from gum benzoin, or be prepared by oxidizing benzaldehyd, benzyl alcohol, or toluene.

Properties.—It forms white glistening plates which sublime at 100° C. (212° F.), melt at 120° C. (248° F.), boil at 250° C. (482° F.). Its vapor, derived from benzoin, has an aromatic odor, but the synthetic acid is odorless. Sparingly soluble in cold water, it dissolves readily in hot water, alcohol, and ether. As a monobasic acid it forms but 1 series of salts, such as the official benzoates of sodium, lithium, calcium, and ammonium.

Test.—When benzoic acid or its salts are in neutralized solution they yield to neutral ferric chlorid a red or flesh-colored precipitate of ferric benzoate.

Medical Uses.—The U. S. Board of Food Inspection (1911) regard benzoic acid and sodium benzoate as harmful when used to preserve food. The practice is very extensive in condiments in certain states, but in those states is permitted in quantities not to exceed one-tenth of 1 per cent.; in larger amounts it is condemned. Benzoic acid is an antiseptic and antipyretic. Given in full doses, it increases the acidity of the urine by its conversion in the body into hippuric acid. It is used to correct the alkaline urine of cystitis. *Dose*: 5 to 20 gr. (0.3–1.25 gm.).

Excretion of Cyclic Compounds.—Aromatic bodies are very stable, owing to the resistance offered to oxidation by the benzene nucleus. Once absorbed, the nucleus persists, though when eliminated it has formed a new combination. In another place (p. 459) it has been stated that phenol containing the OH benzene ring is absorbed by the intestines and passes out by the kidneys as an acid ester, either as potassium sulphophenolate or phenol glycuronate. So benzoic acid having a COOH benzene ring, if it be fed to an animal, is excreted as an amin-ester of glycocoll, viz., hippuric acid, and does not undergo oxidation.

$$\underset{\text{Benzoic acid.}}{C_6H_5COOH} + \underset{\text{Glycocoll.}}{CH_2NH_2COOH} = \underset{\text{Hippuric acid.}}{C_6H_5 . CO . NHCH_2COOH} + H_2O.$$

The suffix *-uric acid* is used to denote a glycocoll amin-ester; thus, salicylic acid escapes from the body as salicyluric acid. This termination merely means that it is an acid in the urine conjugate with glycocoll, not that it is akin to uric acid.

Benzoyl chlorid, C_6H_5COCl, is prepared by the action of hydrochloric acid on benzoic acid:

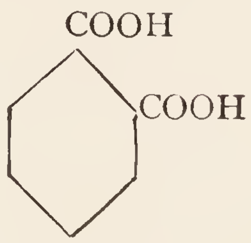
$$C_6H_5COOH + HCl = C_6H_5COCl + H_2O.$$

Its chlorin atom is readily replaced by an alcoholic group to form an ester or by an amino-(NH_2) group to form an amin-ester of benzoyl, $C_6H_5 . CO$. Thus in an alkaline solution:

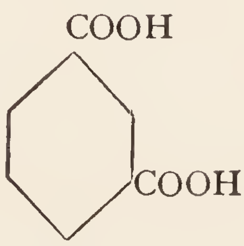
$$C_6H_5COCl + \underset{\text{Ethyl alcohol.}}{HOC_2H_5} = \underset{\text{Benzoyl ethyl ester.}}{C_6H_5COOC_2H_5} + HCl.$$

The alcohol has been *benzoylized.* When the monosaccharids are thus treated they make crystallizable products, proving the presence of an alcoholic or hydroxyl group in their constitution.

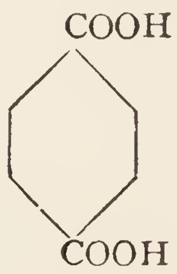
Phthalic Acid ($C_6H_4(COOH)_2$).—The simplest and most important dicarboxylic acids are the 3 whose structure is represented below. They may be prepared by oxidizing the corresponding dimethylbenzenes with nitric acid.



Orthophthalic acid.



Isophthalic acid.



Terephthalic acid.

When strongly heated orthophthalic acid is converted to *phthalic anhydrid*, $C_6H_4<\substack{CO \\ CO}>O$. When this last compound is heated with phenol and zinc chlorid the product is *phenolphthalein*, $C_{20}H_{14}O_4$, water being eliminated. This occurs in yellowish crystals, which when dissolved, 1 per cent., in alcohol make a valuable indicator in alkalimetry. Added to alkaline solutions it forms a salt which imparts a deep-pink color, destroyed, however, by the addition of acids (p. 127). It is a complex derivative of phthalic acid containing three benzene rings. It is given as a painless cathartic and sold under proprietary names as "Purgen," "Laxin," etc. *Dose*: 1–5 gr. (0.06–0.30 gm.). "Phthalins" are a different group of little importance made by the reduction of the phthaleins.

Phenolsulphonephthalein, $C_6H_4CO \cdot SO_2(C_6H_4OH)_2$, differs from the above in that a CO group of the latter is replaced by an SO_2 group. It is a light red crystal soluble with difficulty in water, but readily in alkalis and alcohol. It is non-poisonous, and is used subcutaneously as a soluble monosodium salt to test the functional activity of the kidneys (p. 595). It is readily absorbed and excreted mainly in the urine.

HYDROXY- OR PHENOL ACIDS

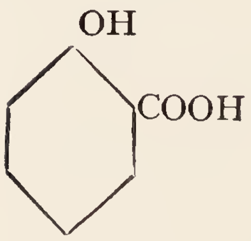
These are derived from benzoic acid and its homologues as glycollic acid is from acetic acid—that is, by substitution of hydroxyl for hydrogen. When that group is united to the carbon of the nucleus, the compound has something of the character of phenols. Thus, the 3 isomeric *hydroxybenzoic acids*, $C_6H_4(OH).COOH$, are not only carboxylic acids (having $-COOH$), but are also phenols (having $-OH$). This class includes the important acids—salicylic, gallic, and tannic.

They may be obtained indirectly from benzoic acid or its homologues by the same reactions given for the preparation of phenol from benzene—that is, first, a nitro-compound; second, reduction to an amido-compound; and, finally, treatment with nitrous acid.

Another synthetic method is to prepare the aldehyd by the action of chloroform on the corresponding phenol in the presence of caustic soda. Exposure to the air oxidizes the aldehyd into the acid.

The hydroxy acids are colorless, crystalline, and soluble in water. They form salts when treated with metallic carbonates or hydroxids; the hydrogen of the carboxyl, $-COOH$, is displaced, and, with excess of alkali, that of the hydroxyl also.

Salicylic acid ($C_6H_4(OH) . COOH$) (*o-hydroxybenzoic acid*)



occurs in considerable amount in oil of wintergreen (*gaultheria*) as methyl salicylate. It may also be obtained by oxidizing salicyl alcohol or salicyl aldehyd.

Salicylic acid is prepared on a commercial scale as follows: Carbolic acid is treated with caustic soda, forming sodium phenolate. This is saturated with carbon dioxid under pressure, and heated at 200° C. (392° F.) to form sodium phenyl carbonate:

$$\underset{\text{Sodium phenolate.}}{C_6H_5 . ONa} + CO_2 = \underset{\text{Sodium phenyl carbonate.}}{C_6H_5 . O . COONa}$$

By heating this product in the vapor of carbon dioxid under pressure there is a migration of atoms in the molecule, with complete transformation to sodium salicylate:

$$\underset{\text{Sodium phenyl carbonate.}}{C_6H_5 . O . COONa} = \underset{\text{Sodium salicylate.}}{C_6H_4 . OH . COONa}$$

Properties.—Salicylic acid is a white, crystalline solid, odorless, sweetish, and acrid in taste, sparingly soluble in cold, but readily in hot water, alcohol, or ether. It sublimes at 200° C. (392° F.). The monometallic salts, such as sodium salicylate, are soluble; the dibasic dimetallic salts, such as $C_6H_4(ONa) . COONa$, are decomposed by carbonic acid with the formation of the monometallic salt and a carbonate. With neutral ferric chlorid it gives an intense violet color.

Salicylic acid is a valuable antiseptic and antirheumatic, preferable to carbolic acid as a disinfectant because it is odorless.

It is often added to liquors and foods as a preservative. *Dose:* 10 to 15 gr. (0.6–1 gm.) every two hours or less.

Toxicology.—Salicylic acid figures as a poison from accidental overdosing and from its widespread use in preserving food and drink. In the body it becomes conjugate with glycocoll and is eliminated partly as salicyluric acid and partly unaltered (p. 470).

Symptoms.—These are pain and irritation of the pharynx and stomach, difficulty in swallowing, vomiting, diarrhea. The face is flushed and the head feels full, with roaring in the ears. Vision becomes dim and the mind confused, delirious, and, later, comatose. The urine may be albuminous and discolored by hematin. The pulse is weak and breathing labored. When minute quantities are taken daily in food the appetite suffers, digestion is impaired, diarrhea alternates with constipation, eczema appears, the mind is depressed, and the urine may be albuminous.

Fatal Dose.—One ounce (31 gm.) has proved fatal after four days. A less quantity would probably be fatal were the heart or kidneys diseased.

Treatment.—Evacuation and washing out of the stomach should be followed by the free use of raw eggs and milk.

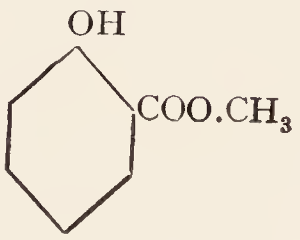
Tests.—Beside the tests given for phenol (p. 461) with bromin water, ferric chlorid, and Millon's reagent, a more characteristic one is used. The material is put in a test-tube with methyl alcohol and one-half as much sulphuric acid. Warmed, cooled, and warmed again, the odor of oil of wintergreen is noted.

To detect salicylic acid in beer, wine, milk, and food: acidify 100 c.c. with dilute sulphuric acid and then extract with equal parts of benzine and ether. Evaporate the extract after separation, and test the residue with ferric chlorid; a violet color is produced.

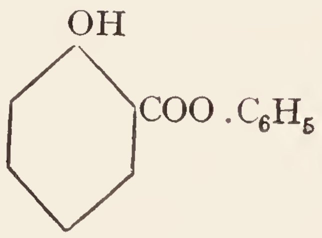
Acetyl-salicylic acid, $C_6H_4 . COOH(C_2H_3O_2)$ (*aspirin*), occurs in white needles, soluble in 100 parts of water, but freely in alcohol and ether. It is used like sodium salicylate for rheumatism in doses of 5 to 20 gr. (0.32–20 gm.). Salicylic acid is set free in the intestines. It is decomposed by heat, moisture, or alkalis.

Novaspirin (*methylene-citryl-salicylic acid*) is a white, odorless, faintly acidulous crystalline powder scarcely soluble in water. It yields 62 per cent. of free salicylic acid in the intestine. Doses of 15 gr. (1 gm.) in a large quantity of warm water are less irritating than aspirin and free from unpleasant secondary effects.

Methyl salicylate $(C_6H_4(OH) . COOCH_3)$ (*artificial oil of wintergreen*) is an ester prepared by distilling a mixture of salicylic acid in methyl alcohol and sulphuric acid. It has the agreeable odor and chemical and antirheumatic properties of the natural oil obtained from plants.



Phenyl salicylate $(C_6H_4(OH) . COOC_6H_5)$ (*salol*) is an ester obtained by heating salicylic acid to 220° C. (428° F.); or by dehydrating a mixture of phenol and salicylic acid. It is a white, faintly aromatic, crystalline powder. Almost insoluble in water, it dissolves readily in ether, chloroform, alcohol, and fatty oils. Passing undecomposed through the stomach, the intestines break it up into phenol and salicylic acid.



It is antirheumatic, antipyretic, and an intestinal antiseptic. *Dose:* 5 to 10 gr. (0.3–0.6 gm.).

Overdoses cause a blending of the poisonous symptoms of salicylic acid and phenol. In the urine will be found both of these agents, detected by the tests given elsewhere.

It is *incompatible* with ferric chlorid, chloral, camphor, bromin water, and carbolic acid.

Salophen $(C_6H_4OHCOO) . C_6H_4NH(C_2H_3O)$ (*acetparamidosalol*).—This is the salicylic ester of 1, 4-acetamidophenol derived from salol, but with acetyl and amino groups.

It contains 51 per cent. of salicylic acid, is a white, tasteless, odorless powder, insoluble in water, but soluble in alcohol and ether. Its action is antirheumatic, antipyretic, and analgesic in doses of 10 gr. (0.6 gm.). Passing the stomach unchanged, it breaks up in the intestine, liberating salicylic acid and acetylparamidophenol, which is not toxic like the phenol set free from *salol.* Hence its action is akin to that of a mixture of salicylic acid and phenacetin.

Salipyrin (*antipyrin salicylate*) is a white, crystalline powder without odor, but with a sweetish taste. It is sparingly soluble in water, alcohol, and ether. It is prepared by direct union of salicylic acid and antipyrin, and is an antirheumatic and analgesic.

Dose: 15 gr. (1 gm.).

Salicylsulphonic acid, $C_6H_3(OH) . SO_3H . COOH$, is a crystalline substance used in testing for albumose in urine (p. 636). It does not precipitate urates or resins, but throws out all proteins. None of the proteins precipitated redissolves on heating except albumose.

Gallic acid $(C_6H_2(OH)_3COOH)$ (*trihydroxy-benzoic acid*) is found in tea, nutgalls, and other astringent vegetable products. It is prepared by boiling tannic acid with dilute acids, so as to hydrolyze it:

$$\underset{\text{Tannic acid.}}{C_{14}H_{10}O_9} + H_2O = \underset{\text{Gallic acid.}}{2C_7H_6O_5}$$

It is a white, crystalline solid, melting at 215° C. (419° F.) to form pyrogallic acid and carbon dioxid. It is soluble in water, imparting an acid reaction and an astringent taste. It is a reducing agent, precipitating metallic gold, silver, and platinum from solutions of their salts. With ferric chlorid it gives a bluish-black precipitate. A deep rose color develops when its solution is treated with a piece of potassium cyanid.

Dose: 5 to 20 gr. (0.3–1.25 gm.). It is *incompatible* with ammonia, lead acetate, opium, silver salts, ferric salts, potassium chlorate, and permanganate.

Dermatol is the trade name for a basic gallate of bismuth used as an antiseptic dusting-powder.

Tannic acid $(C_{14}H_{10}O_9 = (C_6H_2)_2 . (OH)_5O . CO . COOH)$ (*tannin, digallic acid*) occurs in tea leaves, in the bark of trees, and in large amounts in nutgalls, from which it is obtained by extraction with boiling water, alcohol, or ether. It is usually prepared

in light-yellow, amorphous scales which have a very astringent taste and characteristic odor. It is easily soluble in water, giving an acid reaction, and with ferric chlorid a blue-black or dark-green color. The fact that hydrolysis converts it completely into gallic acid shows that it is an anhydrid of that acid.

Tanning is the art of making leather from prepared animal skins or membrane by immersion in a solution of tannic acid or a mixture of astringent bark. The animal substance absorbs and combines with the tannin, changing to leather, which is tougher, does not putrefy when moist nor grow hard and horny when dry.

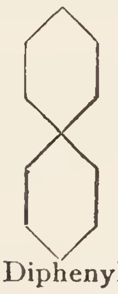
In medicine tannic acid is valued as an astringent and styptic. *Dose*: 2 to 10 gr. (0.13–0.6 gm.). It is present in the preparations: *glycerite* (20 per cent.); *styptic collodion* (20 per cent.); *ointment* (20 per cent.); *troches* (1 gr. each).

Its *incompatibles* are the salts of iron, lead, mercury, antimony, copper, and silver; alkaloids, gelatin, albumin, starch, iodin, iodoform, lime water, spirits nitrous ether, chlorates, and permanganates.

Tests.—Ferric chlorid gives a deep blue precipitate which redissolves in excess, changing to a green color. Potassium hydroxid yields with it a brown color. A weak solution of tannic acid, treated gradually with lime-water, precipitates white, changing to blue and green.

POLYNUCLEATED COMPOUNDS

The compounds hitherto studied have but *one* benzene nucleus or closed chain of 6 carbon atoms. They may be regarded as simple derivatives of benzene, being easily prepared from it and reconverted to it. There are others, however, which are also derivatives of benzene, but which are in a class of aromatic hydrocarbons containing *two* independent closed chains joined at one point, like diphenyl, or even *three*, like triphenyl-methane.



Diphenyl.

In the fatty series ethane, C_2H_6, is sometimes considered as having 2 methyl groups, $CH_3 . CH_3$, and called *dimethyl*. So it is that phenyl, C_6H_5, uniting directly with another phenyl group,

forms the hydrocarbon *diphenyl*, $C_6H_5-C_6H_5$, which is not, however, a homologue of benzene. This and other hydrocarbons, such as naphthalene and anthracene, form the starting-points of new homologous series, and become the parents of a large number of derivatives.

Diphenyl, $C_6H_5-C_6H_5$, is prepared by removing with sodium the bromin of brombenzene in ethereal solution:

$$2C_6H_5Br + 2Na = C_6H_5 . C_6H_5 + 2NaBr.$$

It is a colorless crystalline substance, which when oxidized forms benzoic acid with destruction of 1 benzene nucleus. It forms a whole class of substitution derivatives, of which one is diphenylamin. This, dissolved in strong sulphuric acid, is a delicate test for nitric acid, turning blue with a trace of acid or nitrate.

Naphthalene, $C_{10}H_8$ (*naphthalin*), is second only to benzene in its economic importance. Like anthracene, it is the point from which dyemakers start in the production of a large number of valuable colors. It is more abundant in coal-tar than any other hydrocarbon. Its crude crystals are deposited on cooling the fractional distillate of coal-tar, boiling between 180° and 220° C. (356° and 428° F.). The impurities are made non-volatile by the addition of sulphuric acid, the pure volatile naphthalene being then separated by sublimation.

It forms in large, colorless, lustrous plates, melting at 80° C. (176° F.) and boiling at 218° C. (424° F.). It is extremely volatile at all temperatures, giving off a penetrating, peculiar, but not ill-smelling vapor. This vapor mixed with coal-gas gives increased illuminating power. Almost insoluble in water, it dissolves easily in hot alcohol and ether. It is largely used under the names of *moth balls*, *white tar*, and *mineral camphor*, to prevent the destruction of wool and fur clothing by moths. Its chief use is in making the naphthalene dyes.

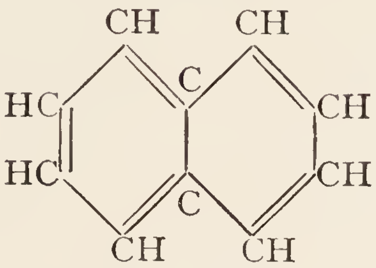
It is used in medicine as an antiseptic and parasiticide. *Dose:* 5 to 10 gr. (0.3–0.6 gm.).

Toxicology.—Given to lower animals, naphthalene causes diarrhea and wasting, with cataract and other changes in the eye.

Symptoms.—Poisonous doses are followed by distress of the stomach, vomiting, colic, and purging. Eliminated by the kidneys, it causes pain in the back and over the bladder, with albuminous and dark-colored urine.

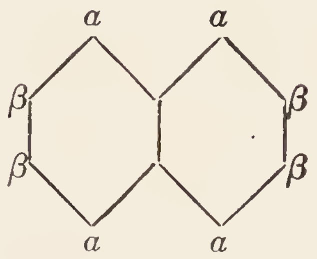
Tests.—Naphthalene is dissolved out of a distillate by means of ether. Picric acid yields with it yellow crystals. A fragment dissolves in chloral without change of color, after warming on a water-bath. On adding to this a few drops of hydrochloric acid and warming, the mixture turns to a rose color, changing to violet or brown on the addition of zinc.

Constitutional Formula.—All the experiments to ascertain the structure of the naphthalene molecule, $C_{10}H_8$, point to the conclusion that it and its derivatives are best explained when its constitution is expressed by two closed chains of 6 carbon atoms, so condensed that they have 2 carbon atoms in common, as shown by the double hexagon below:



Naphthalene, $C_{10}H_8$.

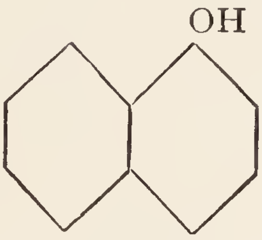
or simply



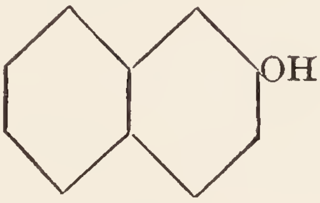
Alpha and *beta* positions.

To account for 2 isomeric monosubstitution products of naphthalene, use is made of the fact that the 8 hydrogen atoms have not all the same relations to the rest of the molecule. For example, the four α positions are identical, so are the four β positions; but the one set differs relatively from the other. This accords with the fact that there are 2 monochlornaphthalenes, 2 monohydroxynaphthalenes, etc. At any angle marked α the substituting atom is in union with a carbon atom common to both hexagons, while those marked β are not so placed.

Naphthol ($C_{10}H_7OH$).—The two monohydroxy-substitution derivatives of naphthalene are known as *alpha*-naphthol and *beta*-naphthol. Their constitution is shown by the duplicated rings:



α-Naphthol.



β-Naphthol.

These correspond with monohydric phenols and are of great importance in dye-making. They are both derived from coal-tar or naphthalene, and have color reactions with ferric chlorid and behave in other ways like the phenols. Both are colorless and crystalline, with a faint odor recalling that of carbolic acid, and a burning and acrid taste. *Beta-naphthol* is readily soluble in hot water, which is not the case with *alpha-naphthol*. *Betanaphtholum*, U. S. P., is an intestinal antiseptic and parasiticide. *Dose:* 5 to 10 gr. (0.3–0.6 gm.).

The hydrogen of the hydroxyl may be replaced by metals, giving rise to a class of *naphtholates*, such as that of bismuth and that of sodium, $C_{10}H_7ONa$ (*microcidin*).

Experiment.—Molisch's Test for Sugars.—If a carbohydrate in solution be treated with an alcoholic solution of α-naphthol and

a few drops of sulphuric acid added carefully to form a bottom layer, a violet band due to furfurol appears at the line of contact. This reaction reveals sugar even when in combination with proteins, as in glucosamin.

Toxicology.—At one time beta-naphthol was used as an alcoholic solution or ointment, applied to the skin to cure scabies. After such applications there have been in some cases eczema, retinal changes, acute nephritis, and death. One dram (3–4 gm.) in the form of ointment was fatal to a pregnant woman in twenty-five hours.

Treatment.—The symptoms call for the same procedures as are used for phenol-poisoning (p. 460).

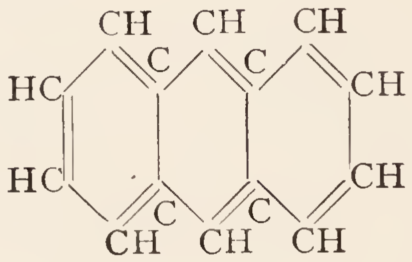
Detection.—The suspected material is shaken with alcohol and the extract evaporated to a residue. This, warmed with potassium hydroxid and chloroform, yields a blue color.

Aluminium naphthol-disulphonate (alumnol) is a salt of the dibasic acid, $C_{10}H_5(OH)(SO_3H)_2$, derived from naphthol by the action of sulphuric acid. *Naphthosalol* is salicylate of β-naphthol or *betol.*

Anthracene ($C_{14}H_{10}$).—As the starting-point in the synthesis of *alizarin* (*artificial madder*) and *turkey-red dye*, anthracene is prepared extensively from the *green oil* of coal-tar. It crystallizes in colorless, lustrous, fluorescent plates, soluble in hot benzene.

Constitutional Formula.—There is evidence that the molecule of anthracene is composed of *condensed* nuclei, and experience shows that the facts can be accounted for if its constitution be regarded as consisting of 2 benzene residues linked by 2 CH groups or 3 hexagonal rings. Thus:

$$C_6H_4\left\langle\begin{matrix}CH\\|\\CH\end{matrix}\right\rangle C_6H_4 \quad \text{or}$$



Phenanthrene ($C_{14}H_{10}$).—Coal-tar yields this isomer of anthracene. It appears to be diphenyl in which the 2 benzene residues are united at the ortho-positions by the group $-HC{:}CH-$ thus: $H_4C_6\text{-}HC{:}CH\text{-}C_6H_4$. It is formed as a condensation product after the vapor of benzene compounds has passed through a red-hot tube. It is found as a nucleus in the alkaloids morphin and codein.

Anthraquinon ($C_6H_4<^{CO}_{CO}>C_6H_4$) (*Diphenylene-diketone*).—When anthracene is treated with nitric acid it does not yield a

nitro-derivative: it is oxidized to anthraquinon, $C_{14}H_8O_2$, 2 atoms of hydrogen being displaced by 2 atoms of oxygen.

It crystallizes in yellow needles, and when acted on by sulphuric acid and then by soda and potassium chlorate yields, by complex processes, *alizarin* or dihydroxyanthraquinon, $C_6H_4<\substack{CO\\CO}>C_6H_2(OH)_2$. This is the active color principle of the madder root. It produces various colored compounds with metallic oxids; for example, with aluminium, a fast red, *turkey red;* with lime, blue; with a ferric salt, dark purple.

Alizarin monosodium sulphonate is the yellow reagent used by Töpfer as an indicator for uncombined acids of the gastric juice, excess of caustic soda turning the tested fluid pure violet by the formation of the disodium derivative, $C_6H_4<\substack{CO\\CO}>C_6H_2(ONa)_2$ (Plate 6, B, B′).

NITROGEN DERIVATIVES OF BENZENE

An important class of compounds results from the ease with which *nitro-* (NO_2), *amido-* (NH_2), and *diazo-* (N_2) groups are substituted for the hydrogen of the benzene nucleus. The *nitration* of many aromatic compounds is accomplished by solution in nitric acid. When not soluble in nitric acid, the process is facilitated by using a mixture of strong nitric and sulphuric acids. As a rule, a high temperature and concentrated acids cause the substitution of several nitro-groups. Generally speaking, the nitro-compounds are crystalline and yellowish, insoluble in water, but soluble in benzene, ether, and alcohol.

Nitrobenzene ($C_6H_5 . NO_2$) (*Essence of Mirbane*).—When benzene (10 c.c.) is slowly treated with a mixture of nitric acid (12 c.c.) and sulphuric acid (16 c.c.), and the vessel kept cool by immersion in water, the benzene dissolves. When poured into water a yellow oil sinks to the bottom. This is nitrobenzene, and the reaction is as follows:

$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O.$$

Nitrobenzene is insoluble in water, has a specific gravity of 1.2, is sweetish in taste, and has a strong odor, resembling oil of bitter almond, for which oil it is often substituted in flavors and perfumes, notwithstanding its poisonous character. Its chief use is in the manufacture of anilin.

Toxicology.—It breaks down the blood-corpuscles, forms methemoglobin (Plate 4, Fig. 1, d), and paralyzes the nerve centers.

The resulting symptoms may not be noticeable for several hours, when suddenly the face becomes livid, the nails bluish, the pulse feeble, the skin cold; giddiness and vomiting may lead quickly to coma, sometimes complicated with convulsions, and often ending in death from apnea. If death is not prompt, the case may be complicated by jaundice. The same symptoms, resembling those caused by hydrocyanic acid, have been induced by inhalation of the vapor in the industries using nitrobenzene.

Fatal Dose and Period.—Death would probably be caused by 30 drops to 1 dram. Coma usually appears in four hours, with death two hours later.

Treatment.—Using a siphon tube, the stomach should be washed out with warm water freely. Strychnin, digitalis, and artificial respiration are useful to sustain the heart and respiration. Alcohol by the stomach must be avoided, as it favors absorption.

Postmortem Appearances.—These include a persistent odoi of bitter almond and oily drops of the nitrobenzene in the alimentary tract. The blood is chocolate-colored and fluid.

Detection.—(1) Nitrobenzene is dissolved in warm alcohol and reduced to anilin by adding powdered zinc, followed by single drops of hydrochloric acid to evolve hydrogen until no odor of nitrobenzene is left. The solution, diluted and made alkaline, is extracted with ether and the residue tested for anilin (p. 482).

(2) A few grains of potassium hydroxid mixed with 3 drops of water and 2 drops of carbolic acid are boiled in a dish and then a few drops of the suspected material is added. After boiling, a red ring appears at the edge, the red changing to green when calcium hypochlorite is added.

AROMATIC AMIDO-COMPOUNDS AND AMINS

In another place (p. 500) the amids and amins of the fatty series are referred to as ammonia, in which the hydrogen atoms have been displaced by fatty radicals. Analogous compounds are made when the radicals substituted are aromatic, such as *amidobenzene*, $C_6H_5 . NH_2$, and *benzylamin*, $C_6H_5 . CH_2 . NH_2$. Those which, like amidobenzene, have the amido-group united directly with the nucleus are called *amido-compounds;* those containing that group in the side chain, like benzylamin, are called *aromatic amins*, and are of very little importance.

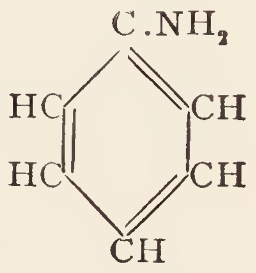
Preparation of amido-compounds in general is performed by reducing the nitro-compounds with nascent hydrogen, a metal, or stannous chlorid. Thus:

$$\underset{\text{Nitrobenzene.}}{C_6H_5NO_2} + 6H = \underset{\text{Amidobenzene.}}{C_6H_5 . NH_2} + 2H_2O.$$

The **properties** of the amido-compounds are similar to those of the primary amins. The basic character of ammonia is diminished by the substitution of phenyl, C_6H_5-, which is not the case with the fatty amins. Warmed with nitrous acid in solution, they yield phenols, as the fatty amins under like conditions form alcohols:

$$\underset{\text{Amidobenzene.}}{C_6H_5 . NH_2} + \underset{\text{Nitrous acid.}}{HNO_2} = \underset{\text{Phenol.}}{C_6H_5 . OH} + N_2 + H_2O.$$

Anilin ($C_6H_5 . NH_2$) (*Amidobenzene, Phenylamin*).—Anilin is contained in coal-tar in small quantities, but commercially it is prepared by reducing nitrobenzene with nascent hydrogen.



When pure, it is a colorless, oily, neutral liquid, with a faint, peculiar odor and a bitter taste. Sparingly soluble in water, it dissolves readily in alcohol and ether. Exposed to light it darkens. It acts as a base, neutralizing acids and forming salts, such as anilin hydrochlorid, $C_6H_5 . NH_2HCl$.

A mixture of chloroform and alcoholic potash heated with one drop of anilin gives the offensive vapor of *isobenzonitril*, $C_6H_5 . NC$. By oxidizing agents, such as arsenic acid, it is converted into *rosanilin*, from which derivatives of various colors are easily produced. This is the basis of the large industry of dye-making. *Rosanilin chlorid*, $C_{20}H_{20}N_3Cl$, forms crystals of a green, metallic luster, which dissolve in warm water to form a deep red solution that dyes fabrics a brilliant magenta. The identity in color of the nitrate and other salts finds explanation in the same colored ion. If the ion be changed by the introduction of methyl for hydrogen, the changes in color range through violet to blue, according to the number of methyl groups.

Pyoktannin-blue is pentamethylrosanilin chlorid, violet in color, soluble, and used as an antiseptic. *Methyl-blue* is the sodium sulphonate of triphenylrosanilin. It is used locally as a disinfectant, but internally is poisonous, having caused death by mistake for methylene-blue, which is less active.

Methylene-blue (*methylthioninæ hydrochloridum*, U. S. P.), is formed by the action of hydrogen sulphid upon an oxidation product of para-amido-dimethylanilin. It occurs in dark green, bronze-like crystals which readily make a deep blue aqueous solution. It is used in dyeing, staining bacteriologic specimens, and internally is given for its analgesic and antipyretic effects. *Dose:* 1 to 3 gr. (0.065–0.2 gm.).

Toxicology.—Anilin poisoning is found in dye-workers who inhale the vapors, but others wearing socks and boots dyed with anilin colors have suffered from absorption by the skin. Like

nitrobenzene, it breaks down the blood and paralyzes the nerve centers. The methemoglobin in the blood imparts a bluish color to the face and finger-nails. The gait is unsteady, the head aches and is dizzy, the pulse feeble, and drowsiness ends in coma. Chronic poisoning causes eczema, anemia, and amblyopia. Anilin is oxidized in the system to para-amidophenol, $C_6H_4 . OH . NH_2$, which is eliminated as a conjugate sulphate. From this the urine takes a dark color and reduces Fehling's solution like glucose. The U. S. Board of Food Inspection (1911) forbids the use in food of any coal-tar dye except those known in commerce as amaranth and erythrosin red; orange I; naphthol yellow S; light green S. F., yellowish; and indigo disulphacid; of the official list.

Fatal Dose and Period.—Death is probable within twenty hours after doses of 1 fl. oz. (30 c.c.).

Treatment.—When the poison has been inhaled, fresh air and stimulants are called for; if swallowed, evacuation of the stomach and bowels, followed by stimulants.

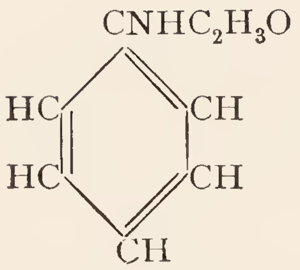
Postmortem Appearances.—There is an odor of coal-tar or anilin in the body, with a brownish color of the blood, due to methemoglobin (Plate 4, Fig. 1, d).

Detection.—1. A solution of free anilin is turned violet by a few drops of fresh calcium hypochlorite. If this be pale, a few drops of ammonium sulphid develops a visible rose color, changing yellow.

2. Sulphuric acid with a trace of anilin turns slowly blue or green when treated with potassium dichromate. The same reagents with strychnin yield a blue, changing to purple and red.

3. One drop of anilin yields with chloroform and alcoholic potash the *isobenzonitril* odor (p. 389).

Acetanilid ($C_6H_5 . NH . C_2H_3O$) (*Antifebrin, Phenyl-acetanilid*).—When the hydrogen of the amido-group in anilin is replaced by acid radicals, the derivative is called *anilid;* for example, acetanilid, formanilid, and oxanilid are anilids prepared by the action of the corresponding acids. When the hydrogen atom is displaced by an alkyl radical, the derivative is known as an alkylanilin; for example, methylanilin, $C_6H_5 . NH . CH_3$.



Preparation.—Acetanilid is prepared by boiling anilin with glacial acetic acid. Anilin acetate is formed and slowly changes, during prolonged boiling, to acetanilid and water. Distillation purifies the acetanilid, which is collected and crystallized in lustrous white plates having a burning taste. It is odorless and is greasy to the touch.

$$\underset{\text{Anilin.}}{C_6H_5 . NH_2} + \underset{\text{Acetic acid.}}{CH_3 . COOH} = \underset{\text{Acetanilid.}}{C_6H_5 . NH . C_2H_3O} + H_2O.$$

Properties.—Acetanilid melts at 113° C. (235° F.). It dissolves sparingly in cold water, but freely in hot water, alcohol, and ether. When heated with acids or alkalis it takes up water, yielding anilin and acetic acid. Its solutions are neutral and are unaltered in color by either ferric chlorid or sulphuric acid.

Acetanilid is anodyne, antiseptic, antipyretic, and antirheumatic. It is the basis of many "headache powders." *Pulvis acetanilidi compositus* contains in 10 gr.: acetanilid, 7 gr.; caffein, 1 gr.; sodium bicarbonate, 2 gr.

Dose: 2 to 10 gr. (0.13–0.6 gm.). It is *incompatible* with alkaline bromids or iodids, forming compounds insoluble in water. It causes spirits of nitrous ether to turn yellow and red. Rubbed with chloral or carbolic acid it forms a soft mass.

Toxicology.—Many cases of poisoning are attributable to the three anilin derivatives—acetanilid, exalgin, and phenacetin—taken carelessly as antipyretics and anodynes. The lowered temperature results from the amidophenol, $C_6H_4<{NH_2 \atop OH}$, formed in the tissues by oxidation of the amidobenzene group, and which is excreted as a sulphate. All of them cause methemoglobin to appear in the blood (Plate 4, Fig. 1, d), producing cyanosis, muscular weakness, dark or bloody urine, nephritis, and jaundice. Very large doses cause sudden profuse perspiration, dizziness, collapse, dyspnea, coma, and convulsions. *Chronic* poisoning from abuse of "headache powder" is characterized by cyanosis, dyspnea, weakness, dyspepsia, anemia, wasting, and dark-colored urine.

Fatal Dose of Acetanilid.—In cases of weak heart or typhoid fever small doses of 10 to 30 gr. (0.6–2 gm.) may cause alarming symptoms. Death has followed 60 gr.

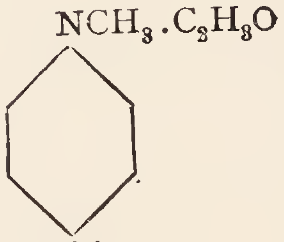
Treatment.—Besides clearing out the stomach and bowels, there is an immediate indication for hypodermic doses of strychnin, followed by normal salt solution, and keeping the recumbent position.

Detection.—1. *Indophenol Reaction.* A gram of acetanilid boiled with 2 c.c. of strong hydrochloric acid and cooled is treated with 2 c.c. of the saturated solution of phenol and a few drops of calcium hypochlorite or chlorin water. The red color thus formed is altered by addition of ammonia to a blue. This test identifies the amidophenol in the urine if performed by the following method: The urine, concentrated on a water-bath, is boiled for three minutes with one-tenth its volume of hydrochloric acid to set free the amidophenol from sulphuric acid. After cooling it is shaken with an equal volume of ether, which is separated and evaporated. The residue, dissolved in water, is treated with a few drops of solution of phenol and some solution of chlorinated lime. The

amidophenol first formed gives a red color of indophenol with the phenol and chlorin, which ammonia changes to blue.

2. Heated with chloroform and alcoholic potash, the *isobenzonitril* odor is developed (p. 380).

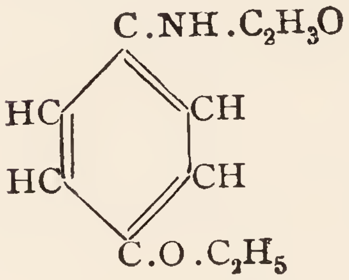
Methylacetanilid ($C_6H_5 . N . CH_3 . C_2H_3O$) (*Exalgin*).—By the action of methyl iodid upon sodium acetanilid the methyl group is substituted for an atom of hydrogen in acetanilid. Methylacetanilid is crystalline, tasteless, faintly aromatic, sparingly soluble in water, freely in alcohol. It is antipyretic and analgesic.



Exalgin.

Dose: 4 to 7 gr. (0.25–0.4 gm.).

Phenacetin ($C_6H_4 . C_2H_5 . O . NHC_2H_3O$) (*Acetphenetidin, Oxyethylacetanilid*).—The effect of reducing agents upon a nitrophenol, $C_6H_4 . OH . NO_2$ is to form the related *amidophenol*, $C_6H_4 . OH . NH_2$. When ethyl is substituted for the hydrogen of the —OH, a corresponding ethylic ether or *phenetidin* is the result, $C_6H_4 . O(C_2H_5) . NH_2$. When paraphenetidin is treated with glacial acetic acid, the acetyl group, C_2H_3O—, is substituted for 1 atom of hydrogen in the —NH_2, and the product is *acetphenetidinum* (U. S. P.).



Its composition differs from that of acetanilid in having oxyethyl, —$O . C_2H_5$, introduced in place of an atom of hydrogen in the nucleus, which causes a slower cleavage into amidophenol.

It is extensively used as an antipyretic, analgesic, and antineuralgic, under the name *phenacetin*. It is a white, odorless, tasteless, crystalline powder, sparingly soluble in water, readily so in alcohol. Cases of poisoning have occurred from overdoses, though it is a safer medicine than acetanilid. The symptoms and treatment are the same as those of acetanilid.

1. *Nitric Acid Test.*—With a few drops of concentrated nitric acid phenacetin yields a yellow to orange-red color. Heat completes the solution, which on cooling gives crystals of nitrophenacetin.

2. *Indophenol Test.*—The same reaction as that of acetanilid, given above. Three per cent. chromic acid may be substituted for the calcium hypochlorite.

Dose: 5 to 15 gr. (0.3–1 gm.). Its *incompatibles* are chloral, carbolic acid, iodin, salicylic, chromic, and nitric acids.

Methacetin [$C_6H_4 . OCH_3 . NH(C_2H_3O)$] (*Oxymethacetanilid*).—The methyl ether of an amidophenol is known as an *anisidin*, $C_6H_4 . OCH_3 . NH_2$. Acted on by glacial acetic acid, this forms

methacetin by the substitution of oxymethyl for an atom of hydrogen in the nucleus and of acetyl in the NH_2.

This substance crystallizes in white, odorless, and tasteless lustrous scales, sparingly soluble in water, readily so in alcohol. It is used as an antipyretic and analgesic.

Dose: 3 to 8 gr. (0.2–0.5 gm.).

DIAZO-COMPOUNDS

When anilin hydrochlorid in very cold solution is mixed with sodium nitrite, and then, by the addition of hydrochloric acid, nitrous acid is liberated in the mixture, a reaction takes place with the formation of diazobenzene chlorid:

$$\underset{\text{Anilin hydrochlorid.}}{C_6H_5 . NH_2 . HCl} + HNO_2 = \underset{\text{Diazobenzene chlorid.}}{C_6H_5 . N_2Cl} + 2HO.$$

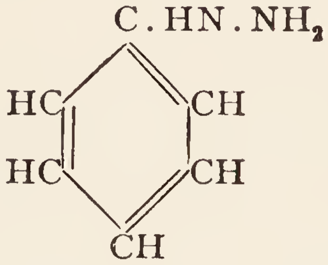
The term *diazo* refers to the 2 atoms of nitrogen linking the phenyl radical to other components: $R-N_2-$. When the free bond is united to acid groups or halogens, the products are called *diazo salts:* $C_6H_5 . N_2 . SO_4H$ is diazobenzene sulphate. They may be regarded as compounds of hypothetic diazobenzene, $C_6H_5 . N_2 . OH$, and its derivatives. These salts, when dry, are unstable to the degree of being explosive. They are colorless, crystalline, and very soluble in water. Their value in industrial chemistry is very great, as they furnish a mother substance susceptible to many reactions, producing a large class of dye substances of varying colors.

Diazobenzene sulphate.

When one bond of each of the 2 nitrogen atoms is united to an atom of hydrogen, a *hydrazo*-compound is formed.

Phenylhydrazin ($C_6H_5 . HN . NH_2$).—This important substance can be prepared by reducing diazobenzene with hydrogen:

$$\underset{\text{Diazobenzene chlorid.}}{C_6H_5 . N_2Cl} + 4H = \underset{\text{Phenylhydrazin hydrochlorid.}}{C_6H_5 . NH . NH_2 . HCl}$$



From the hydrochlorid the free base, phenylhydrazin, is liberated by potash. *Hydrazin*, or *diamin*, is the name given to the group H_2N-NH_2, from which it is assumed these reduction products are derived.

Phenylhydrazin is a crystalline, sparingly soluble, strong base, forming salts with acids. Both base and salts reduce Fehling's solution in the cold. It reacts with aldehyds and ketones to form *hydrazones*, and with grape-, milk-, and malt-sugars to form *osa-*

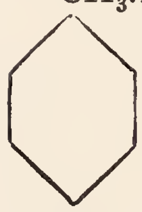
zones. Cane-sugar does not yield an osazone. As these substances are usually crystalline solids of difficult solubility, they are often formed in tests for identifying and isolating aldehyds and sugars. The *osazones* are separated as crystals from aqueous solutions of sugars by boiling with excess of phenylhydrazin hydrochlorid and sodium acetate (Plate 3, *a*, *b*, *c*).

Phenylhydrazin hydrochlorid is a white, changing to a fawn-colored, crystalline powder, with an agreeable odor. It decomposes readily into a dark, offensive paste, which is no longer suitable as a reagent for sugar testing. The crystalline powder should not be permitted to touch the skin, as it may cause an annoying eruption.

Another interesting use of phenylhydrazin is in the manufacture of antipyrin.

Antipyrin ($C_6H_5 . (CH_3)_2 . N_2C_3OH$) (*Phenyl-dimethyl-pyrazolon, Phenazone*).—This is a synthetic base, a derivative of phenylhydrazin, not found in nature, and hence sometimes called an *artificial alkaloid.* It is prepared by treating diacetic ether with phenylhydrazin, making phenyl-methyl-pyrazolon; and then introducing a second methyl group by heating with methyl iodid.

$CH_3.N.N.C_3OH.CH_3$



It is a white, odorless, bitter, crystalline powder, readily soluble in water and alcohol. It fuses at 113° C. (235° F.) and is strongly basic, forming soluble salts. With ferric chlorid it yields a deep red color, and with nitrous acid a bluish green color.

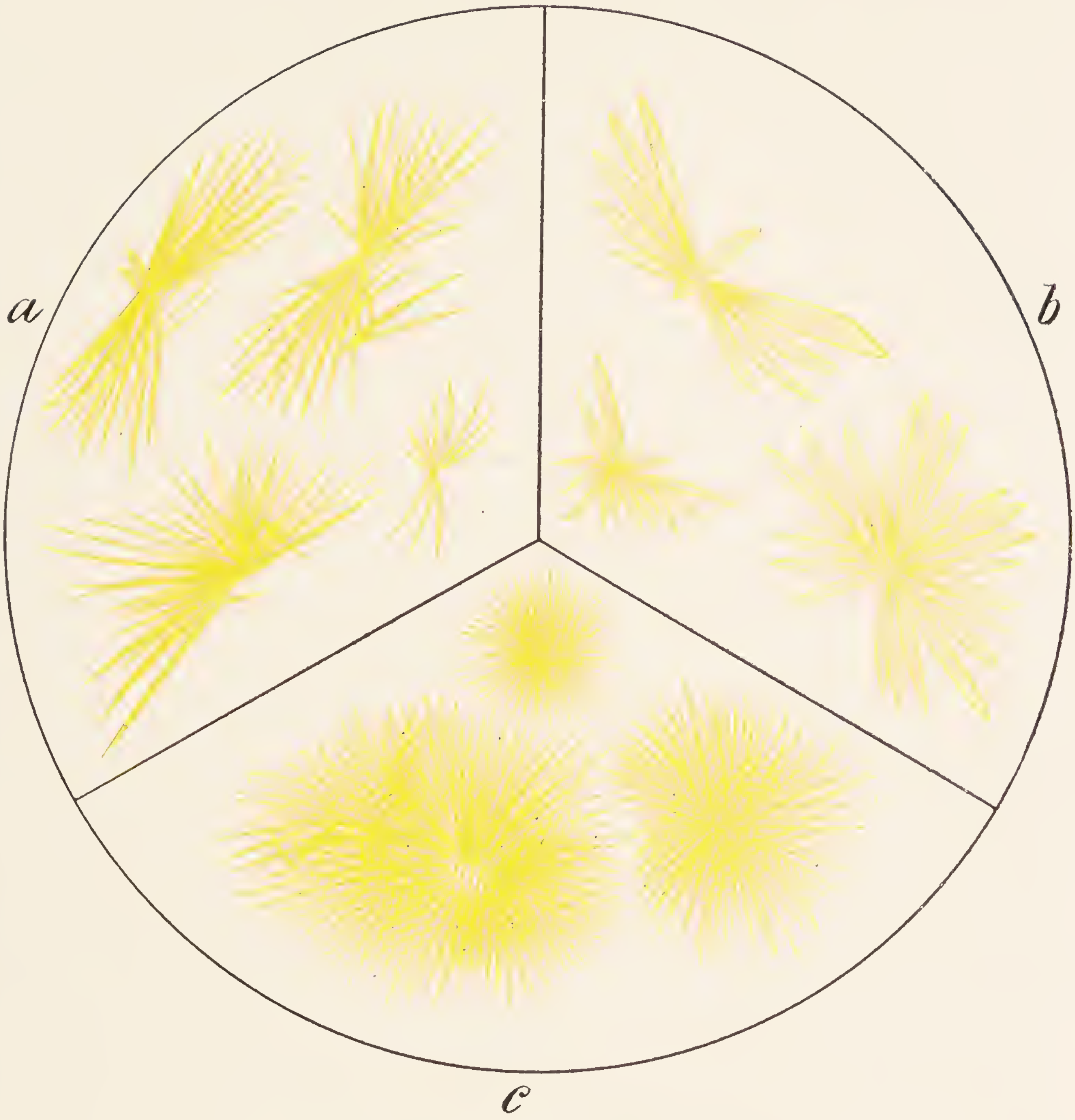
In medicine it is used locally as a styptic and internally as an antipyretic, antirheumatic, and analgesic. *Dose:* 5 to 15 gr. (0.3–1 gm.). It has many *incompatibles:* the halogens, ammonia water, sodium bicarbonate and salicylate, chloral, copper sulphate, chromic acid, iodids, lead subacetate, calomel, mercuric chlorid, alum, carbolic acid, amyl nitrite, benzoates, beta-naphthol, spirits of nitrous ether, quinin, ferric chlorid, tartar emetic, tannic acid, and vegetable astringents. A mixture of antipyrin, calomel, and sodium bicarbonate in water changes the calomel partly to corrosive sublimate, which dissolves, and partly to mercury in the grayish-blue residue. A dose containing 2 gr. of calomel changes enough to yield $\frac{1}{3}$ to $\frac{1}{2}$ gr. of corrosive sublimate—a dangerous quantity.

Toxicology.—Poisoning from antipyrin is nearly always due to the free use of it as a medicine in cases many of which were unfit for it because of defective heart or kidneys.

Acute cases show feeble pulse, difficult breathing, and cyanosis, not so great as that caused by acetanilid. Muscular tremblings may be associated with the stupor, collapse, and coma.

Chronic poisoning from habitual use causes edema of the face, cutaneous affections, indigestion, mental dulness, and anemia.

PLATE 3.



Phenylhydrazin Test for Sugars.

In a test tube put nearly ½ in. (1 gm.) of phenylhydrazin hydrochlorid, an equal quantity of powdered sodium acetate, and enough of the suspected fluid to half-fill the tube. The acetate dissolves as the tube is heated. Boil for 2 minutes and examine after 20 minutes, or, if hurried, examine a drop under the microscope at once without a cover-glass. In 2 or 3 minutes the crystals form: *a*, Sheaves and stars of needles—glucosazone; *b*, rosettes of lance-shaped crystals—maltosazone; *c*, spicules in burr-like clusters—lactosazone.

Fatal Dose.—In patients having heart or lung diseases 20 gr. would be dangerous.

Treatment.—The patient is placed in the supine position and air or oxygen is supplied freely. The stomach is evacuated by emetics or the siphon tube. Ammonia may be inhaled and hypodermic injections given of whisky or strychnin.

Tests.—1. Nitrous acid liberated from a solution of potassium nitrite by sulphuric acid causes with an aqueous solution of antipyrin a blue-green nitroso-antipyrin.

2. Ferric chlorid gives a red color with antipyrin, like that produced with diacetic acid (Plate 8, Fig. 6). The color disappears by the action of mineral acids.

3. Fuming nitric acid, two drops, added to a few drops of solution of antipyrin, gives a green color. After heating this to boiling another drop of the acid produces a red color.

Saccharin ($C_6H_4CO \cdot SO_2NH$) (*Benzosulphinidum, Benzoylsulphonic Imid*).—In making this substance *o*-sulphobenzoic acid is first prepared, and this, treated with ammonia, yields the imid:

$$\underset{\text{Sulphobenzoic acid.}}{C_6H_4 < {SO_2OH \atop COOH}} + NH_3 = \underset{\text{Saccharin.}}{C_6H_4 < {SO_2 \atop CO} > NH} + 2H_2O.$$

It is a white powder with a slight aromatic odor and a remarkably sweet taste, being nearly 300 times as sweet as cane-sugar. It is sparingly soluble in water, but freely so in ether and alcohol. Its solubility is increased by alkaline carbonates, which convert it to *soluble saccharin.*

Experiment.—Its presence is detected by acidulating with sulphuric acid the sugar or other suspected substance and shaking with ether, which does not dissolve sugar, but extracts the saccharin. On separation and evaporation the residue of saccharin is crystalline and sweet.

Uses.—It is used to disguise the taste of unpalatable medicines, and as a substitute for sugar in diabetes, obesity, and gout.

Toxicology.—It retards the action of the enzyms in the digestive fluids and also those of the blood and tissues. Its addition to commercial foods is forbidden by U. S. law (1912).
it depresses general metabolism.

Benzidin ($NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NH_2$) (*p-Diamidodiphenyl*).—This may be compared with two molecules of anilin. It is made by the action of acids, causing an intramolecular rearrangement in *hydrazobenzene*, $C_6H_5 \cdot NH \cdot NH \cdot C_6H_5$. It occurs in colorless, shining plates, is strongly basic, and is used in the preparation of azo-dyes such as *congo-red*, whose sodium salt is a scarlet powder which is turned blue by acids. Benzidin is used in a delicate test for blood (p. 638).

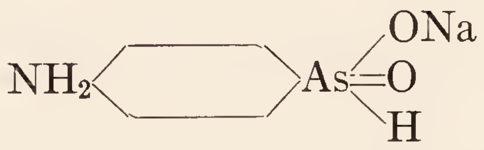
ARSENIC ORGANIC DERIVATIVES

The diazo-compounds react with phenols and amino-compounds to form a class of **Azo**-compounds in which occurs the group $-N=N-$ linking two radicals. They are of importance in dye-making, and have **Azobenzene,** $C_6H_7 . N:N . C_6H_5$, as their parent substance. Nitrogen, phosphorus, and arsenic are sometimes grouped as a family because they have parallel compounds. As we derive *amins* from ammonia NH_3 (p. 532), by substituting alkyl radicals for hydrogen so we can replace the hydrogen of arsin AsH_3 and obtain primary, secondary, and tertiary *arsins*, but unlike amins they lack basic properties. Similar to nitrobenzene, $C_6H_5 . NO_2$, is *arsinobenzene*, $C_6H_5 . AsO_2$, and to azobenzene is arsenobenzene, $C_6H_5 . As:As . C_6H_5$, a yellow, crystalline substance. Corresponding to the dimethyamino-group, $N(CH_3)_2$, is the *dimethylarsino* group in the substance **cacodyl,** $(CH_3)_2As : As(CH_3)_2$, which itself corresponds to tetra-methylhydrazin, $(CH_3)_2N . N(CH_3)_2$.

Cacodylic acid, *dimethylarsinic* acid, $(CH_3)_2AsO . OH$, is crystalline and has salts of medicinal virtue. It is made by oxidizing the poisonous oily mixture which distils when arsenic trioxid is heated with potassium acetate. This liquid has an overpowering odor, from which comes the name (Gr. *kakodes*, ill-smelling) given to its constituents *cacodyl* and *cacodyl oxid.*

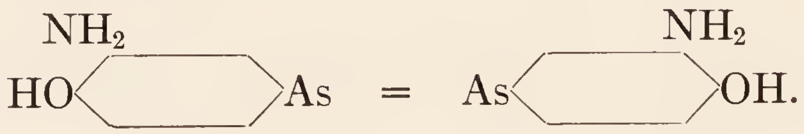
Sodium cacodylate, $(CH_3)_2AsO . ONa,3H_2O$, is a white crystal water soluble, and though it contains arsenic it is much less poisonous than arsenic trioxid (p. 266). These arsenic derivatives of the fatty series are so stable as to lack something of the therapeutic activity shown by the more dynamic compounds derived from the benzene series, such as atoxyl and salvarsan.

Atoxyl (Gr. *atoxikos*, non-poisonous) is the trade name of sodium aminophenylarsonate, a salt of arsenic acid in which anilin is substituted for one hydroxyl group. Its graphic formula is



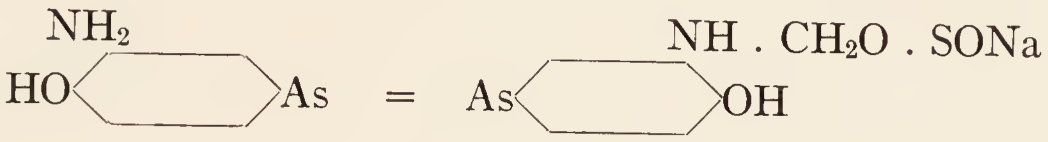
As a bactericide in certain specific infections it is given in comparatively large doses of 6 gr. (gm. 0.4) by hypodermic injection every second day. It dissociates gradually and safely its arsenic as an active ion (p. 288).

Salvarsan (L. *salvare*, to preserve, *sanitas*, health) is the trade name of the hydrochlorid of dihydroxy-diamino-arsenobenzene, which has the constitutional formula,



The NH_2 groups make of it a base capable of union with two acid radicals, while the OH groups confer upon it the ability to unite with bases. By union with 2HCl it forms salvarsan $2(As . C_6H_3 . OH . NH_2 . HCl)$. In water it makes an acid solution which must be carefully neutralized before giving it by intravenous injection. The result is an insoluble suspension. To obviate the difficulty in the technic of administration the following compound has been marketed.

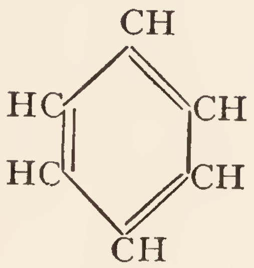
Neosalvarsan is the neutral, water soluble sodium salt of dioxy-diamino-arseno-benzene-monomethane-sulphuric acid, with the formula:



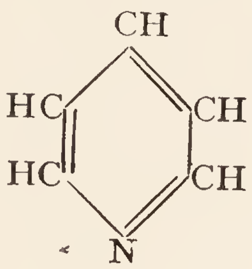
They are best given intramuscularly by injecting through a 20-gage hypodermic needle the warmed contents of an ampule, containing either 0.10 gm. ($1\frac{1}{2}$ gr.) of salvarsan or 0.15 gm. ($2\frac{3}{10}$ gr.) of neosalvarsan, suspended in vegetable fats that are liquid at the temperature of the body.

HETEROCYCLIC COMPOUNDS

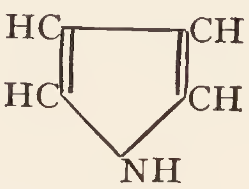
The cyclic compounds previously described have 6 carbon atoms in the ring. As the atoms at the angles are alike, they are called *isocyclic*. If a ring contains fewer than 6 carbon atoms, it is irregular and the compound is called *heterocyclic*. One of the C atoms may be replaced by N, as in pyridin, or the ring may have only 4 C atoms with NH, as in pyrrole.



Benzene.



Pyridin.



Pyrrole.

PYRIDIN AND ITS DERIVATIVES

Among the constituents of coal-tar have been found certain aromatic bases allied to the alkaloids and known as *pyridin bases*. They were first discovered in *bone oil*, a dark brown liquid of disagreeable odor, formed when bones are heated in the preparation of

boneblack. Purified by distillation, this bone oil was at one time used in medicine under the name of *Dippel's oil.*

Pyridin, C_5H_5N, is a product of destructive distillation of many nitrogenous organic substances, and hence found in tobacco smoke. It is prepared by first making nicotinic acid, $C_6H_5NO_2$, by oxidizing nicotin. This, when distilled with lime, yields *pyridin,* as benzoic acid by the same process gives benzene:

$$\underset{\text{Nicotinic acid.}}{C_5H_4N \, . \, COOH} \quad = \quad \underset{\text{Pyridin.}}{C_5H_5N} \quad + \quad CO_2.$$

Many considerations have established the opinion that pyridin, like benzene, has a closed chain or nucleus with trivalent nitrogen substituted for the trivalent group, $CH\equiv$. Its constitution is represented in the formula given above.

Pyridin is a colorless liquid with a pungent, empyreumatic odor and sharp taste, freely miscible with water, alcohol, ether, and oils. Its specific gravity is 1.003, and its boiling-point 116° C. (241° F.). It is a very stable substance of strongly basic properties, alkaline in reaction. It has been used in medicine as a respiratory sedative. *Dose:* 2 to 10 drops.

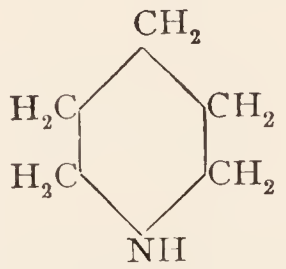
Piperidein (C_5H_8NH).—By the action of nascent hydrogen on the pyridins the several carbon atoms take up additional hydrogen atoms, forming hydropyridins. The best known *tetra-hydropyridin* is the compound piperidein, of which the betel alkaloids are derivatives.

Piperidin ($C_5H_{10}NH$) (*Hexahydropyridin*).—When pyridin is dissolved in alcohol and treated with sodium, piperidin is formed as a reduction product:

$$\underset{\text{Pyridin.}}{C_5H_5N} \quad + \quad 6H \quad = \quad \underset{\text{Piperidin.}}{C_5H_{10}NH}$$

It is reconverted to pyridin on oxidation with sulphuric acid.

It has been shown that the constitution of piperidin is represented by the formula:



Piperidin.

The alkaloid *piperin,* found in pepper, yields piperidin when decomposed by boiling alkalis. Piperidin is a colorless liquid with an odor of pepper. It is miscible with water in all proportions, and

is strongly basic. It behaves like a secondary amin, interacting with methyl iodid to form methylpiperidin, $C_5H_{10}N \cdot CH_3$.

Piperidin and methylpiperidin are the nuclei of a number of vegetable alkaloids. *Coniin*, from hemlock, is a propylpiperidin; the *tropin* of atropin, and *ecgonin* of cocain, are derivatives of methylpiperidin (p. 514).

The Pyridin Homologues.—These are the alkyl derivatives of pyridin: the isomeric *picolins* or *methylpyridins*, $C_5H_4N \cdot CH_3$; the isomeric *lutidins* or *dimethylpyridins*, $C_5H_3N(CH_3)_2$; and the *collidins* or *trimethylpyridins*, $C_5H_2N(CH_3)_3$. They are found in bone oil and coal-tar.

Pyrrole, $\left.\begin{array}{l} HC=CH \\ \;| \\ HC=CH \end{array}\right\rangle NH$ or C_4H_5N, is a constituent of bone oil. It is formed by varied reactions of organic nitrogenous substances, such as albumin and gelatin. It is a colorless liquid, smelling like chloroform and showing feebly basic properties.

It has a homologous series which form substitution derivatives, among which is tetra-iodo-pyrrole, *iodol*, U. S. P., C_4HI_4N, a yellow-brown powder formed by ethereal solution of iodin acting on pyrrole in the presence of oxidizing agents. It is 89 per cent. iodin and is used in medicine as an alterative and antiseptic substitute for iodoform. It is odorless, tasteless, slightly soluble in water, freely in alcohol, chloroform, and oils. *Dose:* 8 to 15 gr. (0.5–1 gm.).

Pyrrolidin, $\left.\begin{array}{l} H_2C-CH_2 \\ \;\;| \\ H_2C-CH_2 \end{array}\right\rangle NH$ (*tetrahydropyrrole*) is made by the action of nascent hydrogen on pyrrole. It stands to pyrrole in the same relation that piperidin does to pyridin. An alkaline liquid, it resembles piperidin in its reaction. It is the nucleus of the hygrin alkaloids and one of the nuclei of nicotin (p. 511).

Prolin or α-Pyrrolidin Carboxylic Acid.—This is produced by tryptic digestion or hydrolysis of casein. It pre-exists in casein as the dipeptid given below:

$$\begin{array}{l} H_3C \\ H_3C \end{array}\!\!>CH \cdot CH_2\underset{\displaystyle NH_2}{\underset{|}{CH}} \cdot CO \cdot N\!<\!\!\begin{array}{l} CH_2 \cdot CH_2 \\ CH \cdot CH_2 \\ | \\ COOH \end{array}$$

The formula is that of a synthetic product of leucin and pyrrolidin carboxylic acid, sometimes called *leucylprolin*.

Piperazin (*Hexahydropyrazin = Diethylenediamin*).—When 2, 3, or 4 nitrogen atoms are present in the benzene nucleus, the compounds are known as *di-*, *tri-*, and *tetrazins*. The diazins are three: *ortho-*, *meta-*, and *para-*, according to the positions of the nitrogen

atoms. Each has a series of substitution derivatives. *Paradiazin,* $\begin{matrix} CH\,.\,N\,.\,CH \\ \| \quad | \quad \| \\ CH\,.\,N\,.\,CH \end{matrix}$, is known under the name *pyrazin.* It is a by-product of alcoholic fermentation, and is found in fusel oil or commercial amyl alcohol.

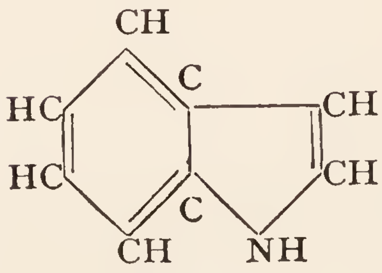
When 6 more hydrogen atoms are taken up by the disengaged bonds, the substance is known as *hexahydropyrazin,* $\begin{matrix} CH_2\,.\,NH\,.\,CH_2 \\ | \qquad\qquad | \\ CH_2\,.\,NH\,.\,CH_2 \end{matrix}$ or $HN : (C_2H_4)_2 : NH$. This substance, called piperazin, may be prepared by reducing paradiazin. It is crystalline, colorless, soluble in water, deliquescent, strongly alkaline, and absorbs carbon dioxid from the air. It combines with uric acid to form piperazin urate, which dissolves in 50 parts of water. It is given as a solvent for uric acid, in the form of citrate and hydrochlorid. *Dose:* 8 gr. (0.5 gm.). It is best given alone, as it is *incompatible* with alum, copper sulphate, ferric chlorid, potassium permanganate, silver nitrate, arsenic, and mercuric iodid, acetanilid, alkaloidal salts, carbolic acid, chloral hydrate, phenacetin, picric acid, quinin, sodium salicylate, tannic acid, spirits nitrous ether.

Indigotin $(C_6H_4{<}{}^{CO}_{NH}{>}C : C{<}{}^{CO}_{NH}{>}C_6H_4)$ (*Indigo Blue*).—This is the blue constituent of ordinary indigo formed from the yellow glucosid, indican, found in certain plants. By heating with dilute acids or by fermentation indican gives indigo blue. Several reactions produce it synthetically—that is, by oxidation of indoxyl or from cinnamic acid.

Indoxyl sulphuric acid is a constituent of the urine, sometimes in such proportion that oxidizing agents give the urine a blue color from the formation of indigo.

When indigo blue is oxidized, it is converted to *isatin,* which is yellowish brown. This property makes it useful as a test for nitric acid. It also loses its color by the action of reducing agents, as in the indigo test for glucose.

Indol $(C_6H_4{<}{}^{NH}_{CH}{>}CH)$ (*Benzopyrrole*).—This substance is a combination of the benzene and the pyrrole rings, as shown by the structural formula. It can be produced synthetically by several reactions. The most interesting method of formation is that by putrefaction of proteins in the intestines during digestion. Part of it remains in the fecal mass and part is absorbed and carried by the portal circulation to the liver to be


Indol.

oxidized to *indoxyl*, $C_6H_4<\genfrac{}{}{0pt}{}{C(OH)}{NH}>CH$. This readily combines with potassium sulphate to form *potassium indoxylsulphate*, $C_6H_4 . NH . CHCKSO_4$. This is the *indican* or *uroxanthin* eliminated by the urine. It is not the glucosid referred to above, but an *ethereal salt* or *conjugate sulphate.*

When hydrochloric acid, with a trace of potassium chlorate or of ferric chlorid, is added to urine, this indican breaks up into potassium sulphate and indigo blue, the latter being formed by oxidation of the indoxyl:

$$\underset{\text{Indican.}}{C_6H_4NH . CH . CKSO_4} + H_2O =$$

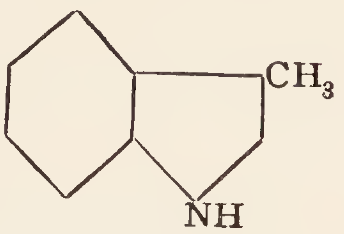
$$KHSO_4 + \underset{\text{Indoxyl.}}{C_6H_4 . NH . C(OH) . CH}$$

$$\underset{\text{Indoxyl.}}{2(C_8H_6NOH)} + 2O = \underset{\text{Indigo blue.}}{C_{16}H_{10}N_2O_2} + 2H_2O.$$

This reaction is made use of in urinary analysis for indican by *Jaffe's method* (p. 596). In testing for indican in the urine by this method the oxidation may be carried too far and the indigo blue be converted to yellowish *isatin.*

The other conjugate sulphates found in the urine in traces are the potassium and sodium compounds of the ester-sulphuric acids of skatoxyl, phenol, catechol, quinol, and paracresol. They vary in amount inversely as the mineral sulphates; and after poisoning by carbolic acid all of the sulphuric acid is taken by the phenol compound at the expense of the mineral sulphates.

Skatol ($C_6H_4<\genfrac{}{}{0pt}{}{C(CH_3)}{NH}>CH$) (*β-Methylindol*).—Skatol is a methyl substitution of indol. The odor characterized as fecal is due to the presence of skatol with indol. The skatol exceeds the indol as a product of the putrefaction of proteins. It can be prepared by the reduction of indigo. Like indol, it is partly absorbed from the fecal mass in the intestines, and is excreted by the kidney as *potassium skatoxylsulphate.*



Skatol.

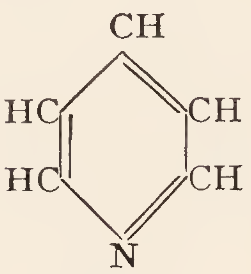
Jaffe's test will yield a red or violet color when the skatoxyl compound is in excess. This color is called *skatol red.* Such urines, when oxidized by nitric acid, turn red, violet, and blue.

Quinolin (C_9H_7N) (*chinolin*) is the parent substance of a group closely related to the vegetable alkaloids and known as the *quinolin* or *benzopyridin bases.* It is in coal-tar and bone oil, can be prepared by distilling quinin and cinchonin with potash, and syn-

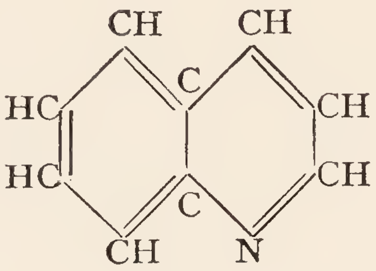
thetically by heating anilin, glycerin, and sulphuric acid in the presence of nitrobenzene.

It is a colorless oil with a characteristic odor, sparingly soluble in water, forming crystalline salts with the acids.

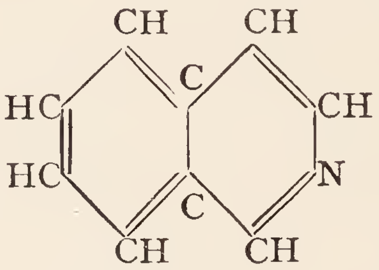
For various reasons the constitution of pyridin, C_5H_5N, and quinolin, C_9H_7N, is believed to have the same relation as that of benzene, C_6H_6, and naphthalin, $C_{10}H_8$, being represented by the formulas below, showing quinolin has a benzene and pyridin ring condensed:



Pyridin.



Quinolin.



Isoquinolin.

Isoquinolin is very like quinolin in chemical properties, but differs physically. It is found in coal-tar with quinolin. In constitution it differs from quinolin in that the benzene ring is attached by the β and γ positions, and not by the α and β, as quinolin.

Thallin ($C_9H_6 . O . CH_3 . N . H_4$ or $C_{10}H_{11}NO$) (*Tetrahydroparamethyloxyquinolin*).—Among the synthetic basic substances made from quinolin and containing its nucleus are *thallin* and *kairin*. Thallin receives its name from the intense green color it forms with ferric chlorid. Its sulphate is in yellowish needles, aromatic, bitter, and soluble in water. In medicine it is used as a transitory antipyretic and antiseptic. *Dose:* 2 gr. (0.13 gm.) hourly.

PURINS AND URIC ACID

Uric acid ($C_5H_4N_4O_3$) (*trioxypurin*) occurs in the tissues of the body, the blood, and the human urine, in small amount, combined with sodium, potassium, ammonium, calcium, and magnesium. It is found as solid ammonium urate in the excrement of reptiles and birds.

Preparation.—Having pulverized the excrement of a serpent, it should be boiled with sodium hydroxid in a porcelain dish until all the ammonia has been driven off. The liquid, having been filtered while hot, is poured into hydrochloric acid. As it cools, a fine crystalline powder of uric acid falls (Plate 7, Fig. 5).

It can be prepared by synthesis by heating urea with glycocoll at 200° C. (392° F.). When decomposed, urea is one of the products. Although uric acid does not contain the acid group COOH, it has 3 groups of HNCO, which give it combining power toward bases and blood-serum.

Properties.—Almost insoluble in water, uric acid is wholly insoluble in alcohol and ether, but soluble in warm glycerin. Its solubility is much reduced when some other acid is present in solution. It is a weak acid with 2 atoms of replaceable hydrogen, forming 2 classes of salts, like the acid sodium salt, $NaC_5H_3N_4O_3$, and the normal sodium salt, $Na_2C_5H_2N_4O_3$. The normal salts are soluble, but the acid salts are soluble to a slight degree only; both are kept in solution in urine by the disodium phosphate. Two salts with organic bases are much more soluble—*piperazin urate* and *lysidin urate;* hence the use of these bases to dissolve uric-acid gravel.

Murexid Test.—In a porcelain dish place some uric acid or a urate. Moisten with nitric acid and evaporate at a gentle heat. If no ammonia be present, a yellow stain of alloxantin is left.

$$\underset{\text{Uric acid.}}{2C_5H_4N_4O_3} + 2H_2O + O_2 = \underset{\text{Alloxan.}}{2C_4H_2N_2O_4} + \underset{\text{Urea.}}{2CON_2H_4}$$

Continued heat splits alloxan into alloxantin, parabanic acid, and carbon dioxid:

$$\underset{\text{Alloxan.}}{3C_4H_2N_2O_4} = \underset{\text{Alloxantin.}}{C_8H_4N_4O_7} + \underset{\text{Parabanic acid.}}{C_3H_2N_2O_3} + CO_2.$$

The yellow residue yields a red-purple color with ammonia, due to ammonium purpurate or murexid:

$$\underset{\text{Alloxantin.}}{C_8H_4N_4O_7} + 2NH_3 = \underset{\text{Murexid.}}{C_8H_8N_6O_6} + H_2O.$$

As xanthin and guanin both yield the red color, add 1 drop of sodium hydroxid and the uric-acid red turns blue. Moisten with water and evaporate to dryness; the color disappears.

Experiment 1.—To a mixture of 50 c.c. of urine and 2.5 c.c. of concentrated solution of sodium carbonate add 5 c.c. of a saturated ammonium chlorid solution. On standing, ammonium urate is precipitated.

Experiment 2.—If a small quantity of uric acid be shaken with water, it does not dissolve. Adding dilute potassium hydroxid, the soluble dipotassium urate is formed. Dilute acid will precipitate uric acid again.

Purin Bodies.—Uric acid is the most highly oxidized member of a series of compounds considered to be derivatives of a synthesized substance, $C_5N_4H_4$, called *purin.* The other members of the series, being basic, are called *alloxuric bases* or *xanthin bases,* after the second member given below. The nucleins found in cell nuclei decompose by acids and enzyms in such a way as to justify

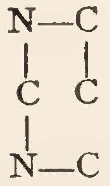
the view that they consist of protein combined with nucleic acid. The nucleic-acid molecule contains some of the purin and pyrimidin bases united with orthophosphoric acid. As purin bodies are products of the decomposition of nucleins, they may be termed *nuclein bases*. They are considered to be intermediate stages of oxidation of nucleoproteins on the way to form uric acid.

Uric acid,	$C_5H_4N_4O_3$	Heteroxanthin,	$C_5H_3(CH_3)N_4O_2$.
Xanthin,	$C_5H_4N_4O_2$	Paraxanthin,	$C_5H_2(CH_3)_2N_4O_2$.
Hypoxanthin,	$C_5H_4N_4O$	Theobromin,	$C_5H_2(CH_3)_2N_4O_2$.
Guanin,	$C_5H_5N_5O$	Theophyllin,	$C_5H_2(CH_3)_2N_4O_2$;
		Caffein,	$C_5H(CH_3)_3N_4O_2$.
Adenin,	$C_5H_5N_5$	Epiguanin,	$C_5H_4(CH_3)N_5O$.

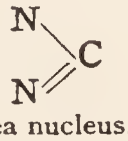
It will be seen that in the second column are the methyl derivatives of the bodies in the first column.

The purin bodies occur together, being found in the same situation and in small amount in the urine, the blood, and many of the tissues. In rare cases the xanthin of the urine separates in the bladder and forms the *xanthin calculus*. They are found in all meat extracts, to which they impart a stimulating quality, but no food value. Some meat extracts contain, in addition, proteins, which are nutritive.

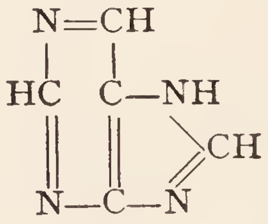
The structure of these bases and their close kinship to uric acid will be better understood if the following graphic formulas are studied. The first two are purely hypothetic bodies:



Alloxan nucleus.

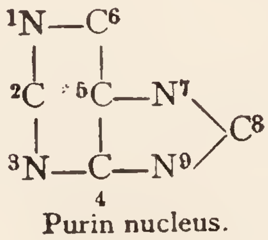


Urea nucleus.



Purin.

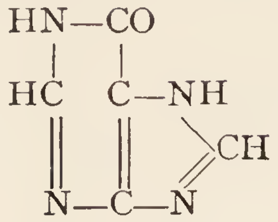
Uric acid and the xanthin bases may be considered as substitution products of purin by the radical hydroxyl, amido-, imido-, or methyl groups. The position of the substituted radicals is indicated according to the numbers in the diagram of the purin nucleus given below. The purin nucleus is made up by joining the carbon-nitrogen nuclei of urea and alloxan given above.



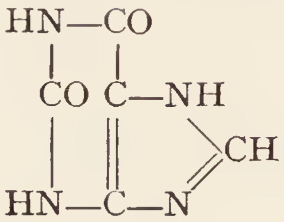
Purin nucleus.

C_5N_4

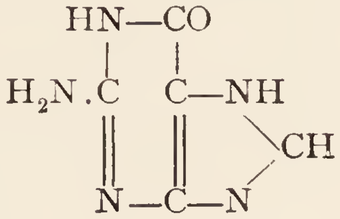
Hypoxanthin is 6 oxypurin:



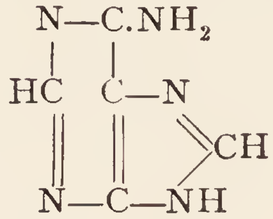
Xanthin is 2.6 dioxypurin:



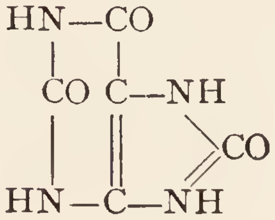
Guanin is 2 amino-, 6 oxypurin:



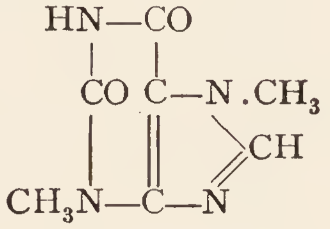
Adenin is 6 aminopurin:



Uric acid is 2.6.8 trioxypurin:



Theobromin is 3.7 dimethyl-xanthin:



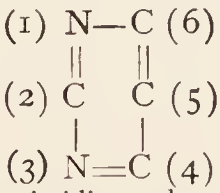
Theobromin, 3.7 dimethylxanthin, $C_5H_2(CH_3)_2N_4O_2$, occurs in the seed of *Theobroma cacao*, from which chocolate is made. *Theophyllin* occurs in tea used as a beverage, and it may be prepared synthetically from dimethyluric acid.

Caffein (*thein, guaranin*), 1.3.7 trimethylxanthin, $C_5H(CH_3)_3$-N_4O_2, is found in tea, coffee, guarana, and other stimulating plants. It may be formed from trimethyluric acid. It is soluble in 80 parts of water, 35 of alcohol.

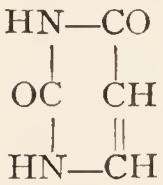
Caffein citrated contains 50 per cent. of caffein. It is a white powder with an acid taste, soluble in 25 parts of water. *Dose:* 2 to 10 gr. (0.13–0.65 gm.).

Murexid Test.—To 0.5 gm. of caffein in a porcelain dish add a few cubic centimeters of strong fuming nitric acid and evaporate to dryness. A yellow stain is left, which on moistening with ammonium hydroxid becomes purple.

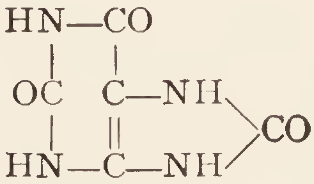
Pyrimidin Bases.—When the nucleic acids break up, the products are the purins referred to above and the bases uracil, thymin, and cytosin, which are derivatives of pyrimidin, $C_4H_4N_2$. Pyrimidin is obtained by splitting off one side of purin. Uric acid can be formed synthetically from these derivatives. The relationship is expressed in the following formulas:



Pyrimidin nucleus.



Uracil.



Uric acid.

Uracil, $C_4H_4N_2O_2$, has been found in the nucleoproteins, and so has thymin, $C_4H_3N_2O_2 . CH_3$, which is methyluracil. Cytosin, $C_4H_5N_3O$, is a constant cleavage product of the nucleic acids. It is so intimately related to the purin group that it is supposed to be the mother-substance.

Uric acid in the urine is derived from two sources—the *internal* and the *external*, or *endogenous* and *exogenous*. The *endogenous uric acid* comes from the nucleins of the body cells and their decomposition products, the purin bases. The quantity for each individual is fairly constant and uninfluenced by food. The *exogenous uric acid* arises from the nucleins and purin bases contained in the food. It is, therefore, an addition to the normal quantity and is dependent entirely on the amount of combined and free oxypurins and aminopurins in the food. These are abundant in sweetbreads (thymus gland), liver, kidney, meat soups, peas, beans, asparagus, heavy wines, meats, and fish. A purin-free diet may be made of bread, butter, milk, sugar, eggs, potatoes, rice, and green vegetables. When the diet is regulated so that there are no purins in the food, the output of uric acid is materially lessened. Theobromin, caffein, and other methylpurins in food have no effect on the uric-acid elimination, though they increase the amount of purin bases, such as xanthin and hypoxanthin, in the urine. In the process of metabolism of cell nuclei in the liver, kidney, and other organs, uric acid is a stage between the purin bases and a further oxidation product. This end-product may be urea or allantoin or glycocoll or CO_2 and H_2O.

Nuclein
|
protein——nucleic acid
|
purin and pyrimidin bases——phosphoric acid.

Purin bases are partly oxidized by the liver to
|
uric acid, which is again partly oxidized to
|
urea of urine.

Some of the purin bases, such as adenin, under certain conditions of the body have a marked toxic action. They are supposed to be factors in the production of febrile temperatures. Other nitrogenous waste substances, such as leukomains, creatin, etc., resulting from metabolism of cell protoplasm, have their formation augmented by a diet rich in proteins.

In the urine the ratio of purin bases to uric acid is about 1 : 10. Expressed in terms of the nitrogen content, uric acid N is to that of the purin bases as 4 : 1. The total amount excreted daily varies between 0.0286 and 0.0561 gm.

Hall's Purinometer.—For clinical purposes it is sometimes desirable to determine the total sum of purin nitrogen in the urine,

including that of uric acid. A simple and easy method is that of Walker Hall. His purinometer estimates by volume the amount of silver purins precipitated by ammoniosilver nitrate.

Two solutions are required for solution No. 1 : Mix 100 c.c. of *Ludwig's magnesia mixture*,[1] 100 c.c. of ammonia (20 per cent.), and 5 gm. of finely powdered talc.

Solution No. 2 is a mixture of silver nitrate, 1 gm.; strong ammonia, 100 c.c.; finely powdered talc, 5 gm.; and 100 c.c. of water. No. 1 precipitates the phosphates; No. 2 precipitates the purins, the silver chlorid being kept in solution by the ammonia. The object of the talc is to make the precipitate heavy and definite.

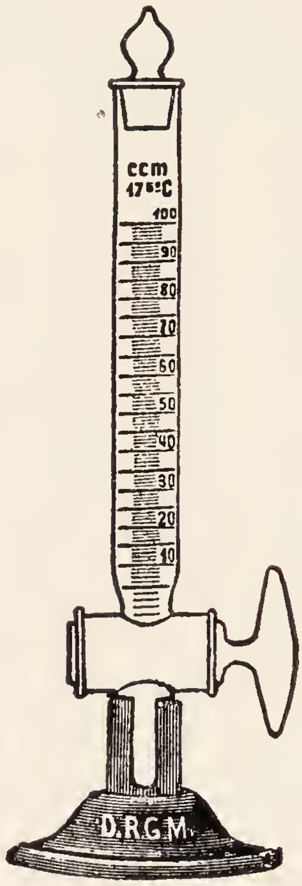


Fig. 82.—Purinometer.

Directions.—Having measured and mixed the total urine of the day, 100 c.c. is made free of albumin (if present) by slightly acidulating, boiling, and filtering. With the stopcock at right angles, 90 c.c. of urine and 20 c.c. of solution No. 1 are poured into the graduated tube (Fig. 82) and the instrument inverted several times. The phosphates are precipitated and the stopcock is opened vertically. In ten minutes the phosphates settle into the lower chamber of the tube and the cock is again turned off at right angles, and No. 2 solution added up to 100 c.c. By free inversion of the tube several times the pale-yellow silver purin is freed of the white silver chlorid. If this does not occur, a few drops of strong ammonia may be added. The instrument is placed in a dark cupboard for twenty-four hours, when the number of cubic centimeters occupied by the precipitate is read off.

A table is furnished with each instrument, which shows the nitrogen percentage yielded by each cubic centimeter of precipitate. This factor, multiplied by the total cubic centimeter of urine divided by 100, gives the total purin-nitrogen.

Example: The silver purin precipitate amounted to 9 c.c. The table stated that 9 c.c. $=$ 0.0175 per cent. purin-nitrogen. The total daily urine was 1210 c.c. Then, $0.0175 \times 12.1 = 0.21175$ purin-nitrogen.

Creatin, $C_4H_9N_3O_2$.—Associated with the purin bases in the nitrogenous extractive of muscular tissue is creatin or methyl-guanidin acetic acid. It is a derivative of guanidin, $NH . C{<}\begin{matrix}NH_2\\NH_2\end{matrix}$,

[1] *Ludwig's magnesia mixture* is composed of magnesium chlorid, 110 gm.; ammonium chlorid, 110 gm.; ammonia, 250 gm.; water, to 1 L. Mix.

which is an oxidation product of guanin. The structural formula of creatin is that of a complex amino-acid.

$$NH \cdot C\begin{matrix} \diagup NH_2 \\ \diagdown N(CH_3) \cdot CH_2 \cdot COOH. \end{matrix}$$

It is easily obtained as a product of metabolism from beef heart or the flesh of fowl by extraction with warm water. As a by-product in making "beef extract" it crystallizes with the residue of meat juice. Boiled with baryta water or other alkali, it breaks up into urea and sarkosin. By prolonged boiling with dilute hydrochloric acid it loses a molecule of water and becomes the anhydrid *creatinin*, $C_4H_7N_3O$, an ingredient of the juice of flesh, also of the blood and the urine. By its reducing action on alkaline copper solution when boiled it is the source of a fallacy in testing for glucose in the urine. Creatinin is a strong base forming a crystalline double chlorid with zinc chlorid in alcoholic solution.

Creatinin is eliminated in a constant amount in the urine for each individual. The muscular strength determines the intensity of the process of metabolism which produces it. With the exception of the acute fevers it is low in pathologic conditions, especially those associated with muscular weakness. In such cases creatin is excreted. It is not present in normal urine.

Allantoin, $HN\begin{matrix} \diagup CO \cdot NH \\ \diagdown CO \cdot CH \cdot HN \cdot CO \cdot NH_2, \end{matrix}$ occurs in the allantoic fluid of cows, the urine of calves, dogs, and cats, newborn children, and pregnant women. It is a product of enzym action on uric acid in liver, spleen, and pancreas. Crystalline and sparingly soluble in water, if heated with alkalis it breaks up to $NH_3 \cdot CO_2$, oxalic and acetic acids.

AMMONIA DERIVATIVES

AMIDS, AMINS, AMINO-ACIDS, AND ALKALOIDS

Ammonia, NH_3, plays a part in organic compounds by the substitution of 1 or more univalent hydrocarbon radicals for an atom of its hydrogen. When the radical is basic,—that is, such as are found in the alcohols,—the product is called an *amin;* when the radical is acid, the compound is called an *amid.*

Amids are neutral in reaction. They are produced when *amidogen*, NH_2, replaces hydroxyl, HO, in a carbon acid. This is the result of a reaction between the HO of the COOH group and NH_3. Thus:

$$\underset{\text{Acetic acid.}}{CH_3 \cdot CO}\boxed{OH \quad + \quad H}NH_2 \quad = \quad \underset{\text{Acetamid.}}{CH_3 \cdot CONH_2} \quad + \quad H_2O.$$

When ammonium acetate, $NH_4C_2H_3O_2$, is heated, H_2O escapes and *acetamid*, $NH_2C_2H_3O$, remains as soluble crystals with a mousy odor. Other atoms of hydrogen may be displaced by reaction with NH_3, and *diacetamid* produced. In a double molecule, $2NH_3$ or N_2H_6, the radical carbonyl may be substituted for 2 hydrogen acids, thus making *carbamid* or *urea:*

$$N\begin{cases}H\\H\\H\end{cases}\qquad N\begin{cases}C_2H_3O\\H\\H\end{cases}\qquad N\begin{cases}C_2H_3O\\C_2H_3O\\H\end{cases}\qquad N_2\begin{cases}CO\\H_2\\H_2\end{cases}$$

Acetamid. Diacetamid. Carbamid.

Amid and Stable Nitrogens.—When an amid is boiled with a caustic alkali, the stronger base displaces the weaker NH_2 from its union with the acid radical. Thus:

$$\underset{\text{Urea.}}{CO(NH_2)_2} + 2NaHO = \underset{\text{Sodium carbonate.}}{Na_2CO_3} + 2NH_3.$$

But the alkali has no affinity with the basic radical in the amins and amido-acids, and hence their nitrogen is not displaced by this means. It is *stable* and requires the action of strong sulphuric acid and potassium sulphate to form ammonium sulphate, as in Kjeldahl's method (p. 366).

Nitrous acid (HNO_2) has the power of substituting OH for and breaking up all NH_2 groups, whether amid, amin, or amido-acids. Thus, if a mixture of ethylamin hydrochlorid, $C_2H_5NH_2$, HCl, and potassium nitrate be added to glacial acetic acid, the nascent nitrous acid causes 2 atoms of nitrogen to be evolved and ethyl alcohol, $C_2H_5 . HO$, is left. Sodium hypobromite, NaOBr, in alkaline solution splits off N from NH_2 groups, but only to the extent of 90 per cent.; hence the calculation of nitrogen contents by this method is not so accurate as by that of Kjeldahl (p. 366).

Urea (*carbonyl diamid, carbamid*) is present in the urine of mammals and of carnivorous birds and reptiles; also in the blood, the muscles, and various animal fluids. Its constitution has been made out by the synthetic reactions given on pp. 193 and 200. It is the chief solid constituent of human urine, and is generated mainly in the liver, from nitrogenous waste substances. The nitrogen of the urea parts from the muscular tissue as ammonium lactate. This $NH_4C_3H_5O_3$ changes in the tissues to carbonate. The ammonium carbonate is dehydrated by the cells of the liver and other organs and tissues, forming first ammonium carbamate and lastly urea:

$$\underset{\text{Ammonium carbonate.}}{CO<^{ONH_4}_{ONH_4}} \text{ less } H_2O \rightarrow \underset{\text{Ammonium carbamate.}}{CO<^{NH_2}_{ONH_4}} \text{ less } H_2O \rightarrow \underset{\text{Urea.}}{CO<^{NH_2}_{NH_2}}$$

It occurs in white or colorless needles with a cool and bitter taste. It melts at 132° C. (270° F.) and readily dissolves in water and

alcohol. When heated to 120° C. (248° F.) in the presence of water it forms ammonium carbonate:

$$CO \,.\, N_2H_4 \quad + \quad 2H_2O \quad = \quad (NH_4)_2CO_3.$$

When heated without water, it breaks up into cyanuric acid and ammonia:

$$3CON_2H_4 \quad = \quad \underset{\text{Cyanuric acid.}}{C_3H_3N_3O_3} \quad + \quad 3NH_3.$$

Fuming nitric acid decomposes it into nitrogen and carbon dioxid:

$$CO \,.\, N_2H_4 + 2HNO_2 = CO_2 + N_2 + 2H_2O.$$

Hypochlorites and hypobromites have a similar effect, giving off CO_2 and N:

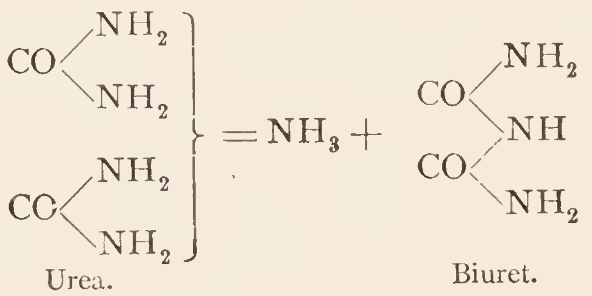
$$CO \,.\, N_2H_4 + 3NaOBr = CO_2 + N_2 + 2H_2O + 3NaBr.$$

If the CO_2 be fixed by passing through alkaline solution, then the free nitrogen may be measured and an estimate made of the quantity of urea required to produce that amount (p. 608).

The solution of urea is neutral in reaction, though its relation to acids is basic. It combines with one equivalent of acids to form salts, the most characteristic of which is *urea nitrate*, $CO(NH_2)_2$, HNO_3, crystallizing in glistening plates. It unites with metals to form such compounds as $HgO \,.\, CO(NH_2)_2$ and $HgCl_2 \,.\, CO(NH_2)_2$.

Tests.—*Nitrate.*—Evaporate fresh urine on a water-bath to a syrupy consistence. On cooling, add strong nitric acid, and crystals of urea nitrate will appear. Having separated the crystals by filtration, they are dissolved in boiling water and the solution treated with barium carbonate. This forms barium nitrate and free urea in the solution, which is then evaporated to dryness and the residue treated with hot alcohol, thus extracting the urea and leaving the barium nitrate. Filtration gives a clear solution which, on evaporation, deposits crystals of urea.

Biuret.—The urea formed above is carefully heated in a test-tube to about 160° C. (320° F.) until no more ammonia comes off. It is then allowed to cool. The residue is a substance called *biuret*, which, if treated with a few drops of potassium hydroxid and of copper sulphate, will yield a violet-red color (Plate 8, Fig. 7):



Urea. Biuret.

Two molecules of urea combine, excluding NH_3 to form biuret.

Urea has diuretic properties esteemed of value in the treatment of dropsies. *Dose:* 10 to 20 gr. every hour in water. It is *incompatible* with chloral hydrate and lead acetate.

Formamid, $N(CHO)H_2$, is a colorless liquid made by heating an alcoholic solution of ammonia with ethyl formate. It unites with chloral, forming *chloralamid*, $N(CHO)H_2C_2HCl_3O$, a recently introduced hypnotic. It occurs in colorless, bitter crystals, soluble in water and alcohol, and decomposable by hot solvents. *Dose:* 15 to 45 gr. It is *incompatible* with silver nitrate and the alkalis.

Amins are said to be *primary*, *secondary*, or *tertiary*, according to the number of atoms of hydrogen in NH_3 which have been replaced by the basic radical. The production is illustrated in the three classes of amins of ethyl, C_2H_5, from ethyl bromid, C_2H_5Br, by the following series of equations:

$$\begin{array}{lll}
C_2H_5Br + NH_3 & = NH_2 . C_2H_5 . HBr \longrightarrow & NH_2 . C_2H_5,\ \text{Ethylamin;} \\
C_2H_5Br + NH_2 . C_2H_5 & = NH(C_2H_5)_2HBr \longrightarrow & NH(C_2H_5)_2,\ \text{Diethylamin;} \\
C_2H_5Br + NH(C_2H_5)_2 & = N(C_2H_5)_3 . HBr \longrightarrow & N(C_2H_5)_3 = \text{Triethylamin.}
\end{array}$$

The salts in the middle column treated with KOH form $KBr + H_2O$ and the amins of the last column.

The following formulas represent the constitution on the ammonia plan:

$$\underset{\text{Ammonia.}}{N\begin{array}{l}-H\\-H\\-H\end{array}} \quad \underset{\text{Ethylamin.}}{N\begin{array}{l}-C_2H_5\\-H\\-H\end{array}} \quad \underset{\text{Diethylamin.}}{N\begin{array}{l}-C_2H_5\\-C_2H_5\\-H\end{array}} \quad \underset{\text{Triethylamin.}}{N\begin{array}{l}-C_2H_5\\-C_2H_5\\-C_2H_5\end{array}} \quad N\begin{array}{l}-CH_3\\-C_2H_5\\-C_4H_9\end{array} \quad \left.\begin{array}{l}\text{Methyl}\\\text{Ethyl}\\\text{Butyl}\end{array}\right\rangle \text{amin.}$$

They are a very important class of basic substances, soluble in water, alkaline in reaction, and have a strong odor similar to ammonia. Like ammonia, also, they precipitate metallic salts and react with acids to form salts without elimination of water.

$$NH_3 \quad + \quad HCl \quad = \quad NH_4Cl.$$

$$\underset{\text{Triethylamin.}}{N(C_2H_5)_3} \quad + \quad HCl \quad = \quad \underset{\text{Triethylamin chlorid.}}{N(C_2H_5)_3HCl}$$

An amin is the result of a reaction between the OH group of an alcohol and NH_3. Thus:

$$\underset{\text{Ethyl alcohol.}}{C_2H_5\vdots OH} \quad + \quad \underset{\text{Ammonia.}}{H\vdots NH_2} \quad = \quad \underset{\text{Ethylamin.}}{C_2H_5 . NH_2} \quad + \quad H_2O.$$

Another view of the constitution of the amins is to consider them as hydrocarbons with the hydrogen replaced by nitrogen

radicals. The primary amins having the amino group NH_2 in them are called *amino-compounds;* thus, methylamin, NH_2CH_3, is amino-methyl. The secondary amins are called *imins* or *imino-compounds*, from the imino group, NH; thus, dimethylamin, $NH(CH_3)_2$, is imino-dimethyl.

Carbylamin or Isonitril Reaction.—When warmed with chloroform and alcoholic potash, ethylamin and all primary amins quickly undergo a change to carbylamins or isonitrils which have an unbearable, characteristic odor:

$$\underset{\text{Ethylamin.}}{C_2H_5 . NH_2} + CHCl_3 + 3KOH = \underset{\text{Carbylamin.}}{C_2H_5NC} + 3KCl + 3H_2O.$$

Trimethylamin is an isomer of propylamin, $N(CH_3)_3$. It is found in fish brine, and is a product of putrefactive decomposition in brain tissue, muscle tissue, and starch paste. In the form of a 10 per cent. solution it is used in the treatment of rheumatism. It is a colorless liquid with a strong, fishy, and ammoniacal odor. *Dose:* 15 to 45 min.

Urotropin (*formin*) is a condensation product when ammonia reacts with formaldehyd, $6CH_2O + 4NH_3 = (CH_2)_6N_4 + 6H_2O$. The odor of formaldehyd disappears in the process. It is *hexamethylenamin*, $(CH_2)_6N_4$, U. S. P. It occurs in soluble crystals, used as a diuretic and solvent for uric-acid concretions. It is said to act as an antiseptic by liberating formaldehyd in the urinary passages. *Dose*: $7\frac{1}{2}$ to 15 gr. ($\frac{1}{2}$–1 gm.) (p. 649).

Amino-acids are regarded as being produced by substituting the amino group, NH_2, for HO in the alcohol group of an oxyacid.

$$\underset{\text{Oxyacetic acid.}}{COOH . CH_2\boxed{OH + H}NH_2} = \underset{\text{Amino-acetic acid.}}{COOH . CH_2NH_2} + H_2O.$$

In reaction they are amphoteric. Since the acid and the base are not in direct union, but joined to different carbon atoms, each group retains its own reaction. They are basic because they have the NH_2, and are acid at the same time because of the COOH group. When chemically inactive these neutralize each other, but acting with outside ions they form anions and kations according to the nature of the exciting ion. They are more stable than the amids and form some optically active physiologic compounds. The protein molecule is composed almost entirely of them, the acid group of one linked to the amino- (basic) group of the next like a train of cars. Their constitution and relation to amids are shown below:

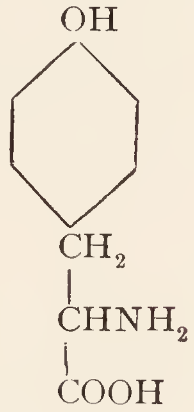
CH_3	CH_3	CH_2OH	$CH_2(NH_2)$
|	|	|	|
COOH	$CO(NH_2)$	COOH	COOH
Acetic acid.	Acetamid.	Oxyacetic acid.	Amino-acetic acid.

As the NH_2 may be joined to any C atom in a chain and with each variation of position make a different compound, the amino-acids are named according to the position in relation to the COOH group, *alpha-*, *beta-*, *gamma-*aminobutyric or other acid (p. 422).

Glycin ($CH_2(NH_2) . COOH$) (*glycocoll, amino-acetic acid*) occurs in animal secretions, usually in combination like uric acid. As *benzoyl-glycin* or *hippuric acid*, $C_6H_5 . CO . NH . CH_2 . COOH$, it occurs in considerable amounts in the urine of herbivora; and to the extent of about 1 gm. daily in human urine. This amount is much increased when benzoic acid and other aromatic substances are taken. Some of the urea made in the liver may be an oxidation product of glycocoll reacting with NH_3. Thus:

$$\underset{\text{Glycocoll.}}{CH_2 . NH_2 . COOH} + NH_3 + O = \underset{\text{Urea.}}{CO(NH_2)_2} + CO_2 + H_2O.$$

Glycin can be prepared as hydrochlorid from hippuric or glycocholic acid by treatment with HCl (p. 469). It contains an amino-group and a carboxyl group, and, therefore, has both acid and basic properties, uniting on the one hand with HCl to make glycin hydrochlorid or, on the other, with NaHO to form sodium glycocollate and water. It is relatively abundant as a nucleus in the proteins. It crystallizes in colorless prisms, soluble in water, giving a red color with ferric chlorid, and with phenol and sodium hypochlorite an intense blue.



Tyrosin.

Other amino-acids of physiologic importance are aminopropionic acid (alanin), aminocaproic acid (leucins), aminoglutaric acid (glutamic), aminosuccinic acid (aspartic), diaminocaproic acid (lysin), diaminovaleric acid (ornithin).

COOH	COOH	COOH	COOH
$CHNH_2$	$CHNH_2$	$CHNH_2$	$CHNH_2$
CH_3	$(CH_2)_3$	$(CH_2)_3$	$(CH_2)_2$
	CH_3	CH_2NH_2	CH_2NH_2
Alanin.	Leucin.	Lysin.	Ornithin.

Alanin is present free in proteins and also in combination with phenol to form tyrosin, and with indol to form tryptophan.

Leucin is very abundant in all proteins, and is one of the end-products of their digestion. Having an asymmetric carbon atom, it has not only the ordinary isomers, but those that are either dextro- or levorotatory.

Ornithin is the precursor of uric acid in its synthesis in birds. It is present in proteins combined with guanidin to form arginin.

Lysin is a product of the tryptic digestion of fibrin. When the protein molecule is attacked by the bacteria of putrefaction, CO_2 is split off from ornithin to form *putrescin;* from lysin to form *cadaverin.* The acid character is lost with the CO_2.

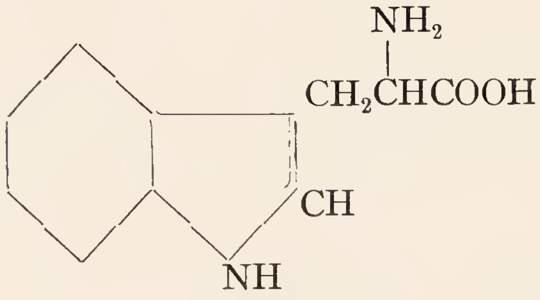
$$\underset{\text{Ornithin.}}{CH_2NH_2 . (CH_2)_2 . CHNH_2 . COOH} = \underset{\text{Putrescin.}}{CH_2NH_2 . (CH_2)_2 . CH_2NH_2} + CO_2$$

$$\underset{\text{Lysin.}}{CH_2NH_2(CH_2)_3 . CHNH_2 . COOH} = \underset{\text{Cadaverin.}}{CH_2NH_2 .(CH_2)_3 . CH_2NH_2} + CO_2$$

In this way other ptomains are formed from other amino-acids by putrefaction (p. 526).

Tyrosin (1:4 *phenolaminopropionic acid*), is a constituent of the protein molecule and is produced by many of its decompositions. It has also been prepared synthetically. Having the HO phenol group, it gives Millon's reaction. While tyrosin is phenol + alanin, it may condense to indol, and indol + alanin become tryptophan. It may therefore be regarded as a binary compound, like tryptophan.

Tryptophan (*β-indol-α-aminopropionic acid*) exists in the protein molecule and is liberated by tryptic digestion. It is the cause of the Adamkiewicz reaction given by proteins (a violet color when treated with sulphuric and acetic acids). It is regarded as the mother-substance of indol, skatol, and skatolcarbonic acid, which are formed from the proteins by the bacteria of putrefaction. In the graphic formula appended its constitution is represented as skatol linked to amino-acetic acid.



Tryptophan.

Glucosamin, $CHO . CHNH_2 . (CHOH)_3CH_2OH$, is an amin in combination with sugar, existing as a component of the protein molecule. Polymeric forms of an insoluble character are called chitosamins, and these mixed with calcium salts make the shells of crustaceæ. Molisch's reaction (p. 477), given by albuminous substances, denotes glucose in the molecule. The large quantities of sugar excreted in diabetes, even when there is no carbohydrate in the food or stored in the liver, is due to the splitting of the glucose nucleus from pure proteins by hydrolysis.

$$C_6H_{11}O_5NH_2 + H_2O = C_6H_{12}O_6 + NH_3.$$

The synthesis of glucosamin proves it to be an intermediate stage between glucose and the *α*-amino-acids, a bridge between carbohydrates and proteins.

Serin and Cystin.—Amino-acids may be derived from oxyacids by substitution of NH_2 in a hydrocarbon group or for alcoholic HO in acids containing more than one such group. *Serin* is α-amino-β-oxypropionic acid ($CH_2OH . CHNH_2 . COOH$), a cleavage product of silk fiber which is a simple form of protein. Closely related to serin is *cystin*, the compound which holds most of the sulphur of the protein molecule. It contains two molecules of *cystein*, which is the acid corresponding to serin:

$$CH_2SH . CHNH_2 . COOH$$

Cystein.

$$HOOC . CHNH_2 . CH_2S . SCH_2 . CHNH_2 . COOH$$

Cystin.

Cystin or α-diamino-β-dithiodilactic acid is formed by hydrolysis of proteins, especially the keratins of hair, horns, and hoof. When produced in the body by metabolism and not decomposed, it is found in the urinary sediment, which may accrete to form the cystin calculus (p. 644). By feeding animals with cystin the amount is increased of *taurin*, $CH_2NH_2 . CH_2SO_3H$, a constituent of the bile acids (p. 566). The easy production of taurin from cystin artificially points to the origin of the bile constituents from the cystin of the protein molecule.

ALKALOIDS

Alkaloids are nitrogenous, organic, principles of alkaline reaction and basic properties. They are found in plants, and in most cases have important physiologic effects. A few alkaloids, such as coniin, nicotin, spartein, are volatile liquids, composed of carbon, hydrogen, and nitrogen only. More than a hundred contain oxygen in addition to carbon, hydrogen, and nitrogen; have a high molecular weight, and are solid, crystalline, and non-volatile.

Generally speaking, the alkaloids, the constitution of which has been established, are tertiary aromatic bases, heterocyclic, containing at least one ring having a nitrogen atom in the nucleus. Exceptions to this are theobromin and caffein, which are purin bases (p. 497).

Many of these alkaloids are known to be derivatives of pyrrolidin, pyridin, piperidin, quinolin, or isoquinolin, and contain the pyridin ring. It is customary to regard them as secondary and tertiary amins, because they have many reactions like ammonia, combining directly with acids to form crystalline salts without elimination of hydrogen or water. Thus:

$$2NH_3 + H_2SO_4 = (NH_3)_2H_2SO_4 \text{ or } (NH_4)_2SO_4.$$

$$\underset{\text{Morphin.}}{2(C_{17}H_{19}O_3N)} + H_2SO_4 = \underset{\text{Morphin sulphate.}}{(C_{17}H_{19}O_3N)_2H_2SO_4}$$

General properties of the alkaloids are as follows:

The liquid alkaloids are volatile, having a disagreeable odor, somewhat ammoniacal; the solid alkaloids are without odor. Generally speaking, the solid alkaloids melt without decomposition when heated carefully above 100° C. (212° F.). A much higher temperature decomposes them. Most of them are white, crystalline, and bitter; and as free bases are sparingly soluble in water, but dissolve readily in alcohol, chloroform, ether, petroleum ether, benzene, and amyl alcohol. On the other hand, their salts (chlorids, sulphates, nitrates, acetates, etc.) are mostly soluble in water or acidulated water, and in alcohol; but, with few exceptions, are insoluble in chloroform, ether, petroleum ether, benzene, and amyl alcohol.

In their physiologic action, as a rule, they display great energy: witness the convulsive effects of strychnin, the coma induced by morphin, the cardiac depression caused by veratrin and aconitin. They are alkaline, unite directly with acids to form soluble salts, and are liberated from this union by the action of alkaline hydroxids and alkaline carbonates, which precipitate them from solution. They are also precipitated by lime, baryta, and magnesia. Other general reagents for precipitating alkaloids, used for their detection and isolation, are phosphomolybdic acid, potassium mercuric iodid, picric acid, tannic acid, and platinum chlorid. Dilute tannic acid and substances containing it, such as strong tea and the vegetable astringents, are used to wash out the stomach as precipitants in alkaloidal poisoning.

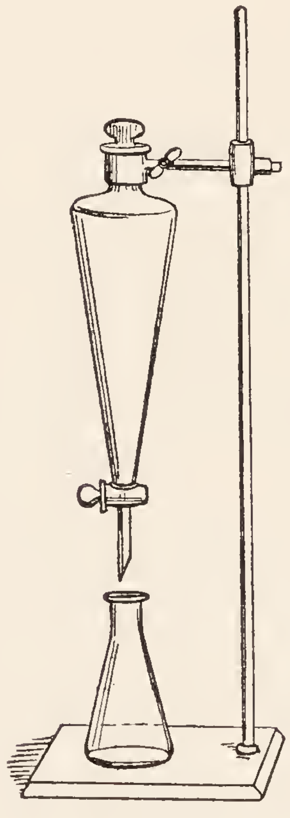


Fig. 83.—Separating funnel.

Characteristic color changes are produced in most alkaloids by oxidizing agents, such as nitric acid, ferric chlorid, potassium dichromate, and sulphuric acid.

Extraction of Alkaloids.—The bark, seeds, leaves, or roots of plants are ground up and macerated with dilute acids, which dissolve out the alkaloids as corresponding salts. This solution, after filtration, is treated with soda to liberate the alkaloid bases. If volatile, the free alkaloids may be distilled off; if non-volatile, the free alkaloids are usually nearly insoluble, and hence are precipitated, to be separated by filtration. To purify them they must be redissolved in acids, again precipitated with alkali, and recrystallized.

If this method does not promise satisfactory results, the alkaline aqueous extract is *shaken out* with chloroform, ether, or other

solvent not miscible with water. The solvent is then put in a *separating funnel* and allowed to form two layers, which are separated by permitting the heavier to flow through the open stopcock into an evaporating dish (Fig. 83). The volatile liquid —chloroform, ether, etc.—used as a solvent is evaporated and the alkaloid is left in the dish.

Antidotes to Alkaloids in General.—The stomach should be washed out through a siphon tube, using freely water, strong tea, or solution of tannic acid, or solution of 10 gr. of potassium permanganate in 16 fl. oz. of water. If the tube be not practicable, vomiting should be induced by teaspoonful doses of mustard or 20-grain doses of zinc sulphate, or hypodermic injections of apomorphin—5 drops of a 2 per cent. solution. After evacuation of the stomach and administration of 10 grains potassium permanganate in a tumbler of water, the dangerous symptoms are combated with remedies which are physiologic antagonists—that is, stimulants, such as whisky and ammonia; artificial respiration, etc.

Detection of Alkaloids in Animal Mixtures.—No operation of the toxicologist demands so much expert skill as that of separating from organic matter an alkaloid in a state so pure as to justify the analyst in swearing to its identity. The technical problem is rendered more complex by the presence, in decaying animal substances, of cadaveric alkaloids or ptomains, behaving chemically, if not physiologically, like the vegetable alkaloids. (For the details of this procedure see p. 528.)

Classification of Important Alkaloids.—The constitution of many alkaloids is as yet undetermined; some of them, however, are known to be derivatives of or to contain the nuclei of the heterocyclic compounds pyrrolidin, piperidin (p. 490), pyridin, quinolin, isoquinolin, and phenanthrene. According to these complex nuclei found in them, the commonly used alkaloids named below are classified as derivatives of—

1. *Pyrrolidin.*—The poisonous hygrins of coca.
2. *Pyridin.*—Pilocarpin of jaborandi.
3. *Piperideïn.*—Arecolin of betelnut, pelletierin of jaborandi.
4. *Piperidin.*—Coniin of hemlock, piperin of pepper.
5. *Pyrrolidin-pyridin.*—Nicotin of tobacco.
6. *Pyrrolidin-piperidin.*—The tropan alkaloids, such as atropin of nightshade, hyoscyamin of henbane, cocain, and ecgonin of coca.
7. *Quinolin.*—The cinchona alkaloids; also strychnin and brucin.
8. *Isoquinolin.*—Narcotin, narcein, papaverin of opium, and hydrastin of yellow root.

9. *Phenanthrene.*—Morphin and codein of opium.
10. *Of Unknown Constitution.*—Veratrin, aconitin, ergotin, gelsemin, physostigmin, and many others.

PYRIDIN ALKALOIDS

Pilocarpin, $C_{11}H_{16}N_2O_2$, is an alkaloid found in jaborandi (*pilocarpus*). Its structure is not perfectly known, but its reactions are those of a compound containing the pyridin ring with the group $C_6H_{12}NO_2$ linked in the β position. Like atropin and cocain, it is an ester decomposed by alkalis. It is crystalline, colorless, soluble, and alkaline. The official salts are the hydrochlorid and nitrate, used as a diaphoretic and miotic. *Dose:* 0.1 to 0.5 gr. (0.005–0.03 gm.) hypodermically. If instilled into the eye to contract the pupil, 1 or 2 drops of a 1 per cent. solution.

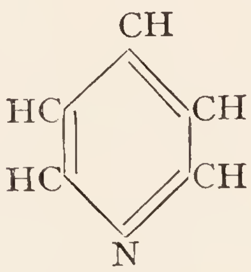
Incompatibles: mercuric chlorid, silver nitrate, tannin, iodids, atropin.

Toxicology.—The symptoms produced by pilocarpin in full doses are copious sweating, salivation, increase of milk and other secretions, contracted pupils, diminished blood-pressure, lower temperature, and prostration.

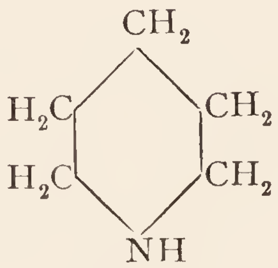
Treatment.—After evacuation of the stomach and washing out with solutions of tannin, the physiologic antagonist is given—atropin, $\frac{1}{60}$ gr., hypodermically. Whisky and ammonia are useful as stimulants.

PIPERIDIN ALKALOIDS

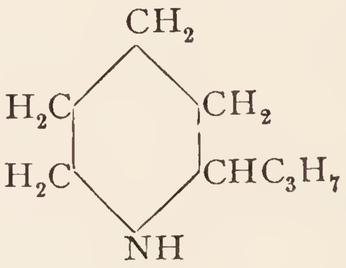
Coniin, $C_8H_{17}N$, is prepared from the fruit of the spotted hemlock by distillation with soda. At first it is a colorless oil, but later changes to brown. It has an acrid taste, a penetrating mousy odor, and is soluble in water. It is strongly basic, forming soluble salts. It is one of the simplest alkaloids in constitution, and the first instance of one prepared synthetically. It is *α-propylpiperidin*, as is shown in these formulas:



Pyridin.



Piperidin.



Coniin.

Toxicology.—*Symptoms.*—Coniin is exceedingly poisonous to the motor centers, a few drops sufficing to paralyze the muscles of respiration in from one to three hours. It produces great prostration, headache, weakness or paralysis of the extremities,

dilated pupils; the intellect remains clear until death occurs by failure of respiration. Two grains would probably prove fatal.

Treatment.—The stomach should be washed out after giving tannic acid or vegetable astringents. The indications are for strong coffee, whisky, and strychnin hypodermically. Artificial respiration may be necessary.

Tests.—(1) The odor is that of a mouse's nest.

(2) Touched with alloxan, coniin develops a purple-red color and white crystals. The crystals, touched with potassium hydroxid, evolve the odor of mice and turn purple.

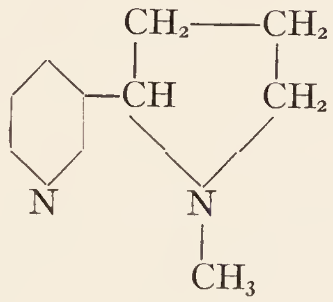
(3) Warmed with potassium dichromate and sulphuric acid, coniin yields butyric acid, detected by its odor.

(4) Coniin placed on the tongue of a small animal causes unsteady gait, paralysis, convulsions, tremor, dilated pupils, and death in a few minutes.

PYRROLIDIN-PYRIDIN ALKALOIDS

Nicotin, $C_{10}H_{14}N_2$, is prepared from the leaves of the tobacco plant by distilling the aqueous extract with milk of lime. Further steps are necessary to render it pure.

It is a colorless oil, turning brown on exposure. It has a burning taste, a pungent, disagreeable odor, like that of an old pipe, and is soluble in water. It is a strong diacid base, forming salts which crystallize. It has been made synthetically, and its constitution has been shown to be a pyridin nucleus joined to a methylpyrrolidin ring, thus:



Nicotin.

Toxicology.—Nicotin is fatally poisonous in doses of 2 or 3 drops of the alkaloid, taken into the stomach. Four drops will kill a dog within five minutes. An infusion or decoction of tobacco leaves is the common form by which nicotin poisoning is induced. It may be swallowed or given by enema, intentionally or by mistake.

The *symptoms* are nausea, vomiting, muscular relaxation, giddiness, numbness, dilated pupils, diuresis, collapse with cold, damp skin, small and thready pulse, and death by heart failure. When the dose is very large, unconsciousness occurs immediately; and after a few respirations death follows within five minutes.

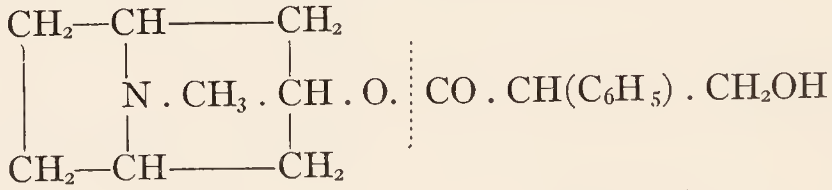
Treatment.—If time permits and there has been no free vomiting, the stomach must be washed out with abundance of warm water or tea. The patient is kept recumbent and warm, while stimulation is practised with whisky or by hypodermic injections of strychnin nitrate, $\frac{1}{25}$ gr.

Detection.—Its reactions are not very characteristic. With nitric acid it gives an orange color; with hydrochloric acid, a violet. Dissolved in ether and mixed with an ethereal solution of iodin, it yields an oily resin of brownish color, which in time forms crystals. Its presence may be detected by the familiar odor of stale tobacco.

PYRROLIDIN-PIPERIDIN ALKALOIDS

Atropin ($C_{17}H_{23}NO_3$) (*Atropia, Atropina*).—From the plants of the Solanaceæ—belladonna, stramonium, hyoscyamus, scopola, and duboisia—are obtained four important alkaloids—atropin or daturin, belladonin, hyoscyamin, and hyoscin or scopolamin.

The *deadly nightshade* (*Atropa belladonna*) contains two alkaloids isomeric and much alike in properties: *hyoscin* and *hyoscyamin.* The latter, when treated with potash, changes to *atropin* by rearrangement of its atoms. All of these and the coca alkaloid, cocain, also contain a methylated pyrrole ring (p. 489) in combination with a piperidin ring (p. 490). Its constitutional formula shows a ring structure like that of cocain, proving it to be an ester of tropic acid and tropin united at the dotted line thus:



Tropin. Tropic acid.

Properties.—Atropin forms glistening prismatic needles, odorless, bitter, almost insoluble in water, but readily soluble in chloroform, alcohol, and ether. It is strongly basic, neutralizing acids, forming salts, of which the *sulphate* is characterized by its ready solubility. *Atropinæ sulphas*, $(C_{17}H_{33}NO_3)_2H_2SO_4$, is either crystalline or amorphous, and is used in medicine instead of the base.

When atropin or hyoscyamin is boiled in baryta water, it undergoes hydrolysis, breaking up into *tropic acid* and the base, *tropin:*

$$\underset{\text{Atropin.}}{C_{17}H_{23}NO_3} + H_2O = \underset{\text{Tropic acid.}}{C_6H_5CH{<}\begin{matrix}CH_2OH\\COOH\end{matrix}} + \underset{\text{Tropin.}}{C_8H_{15}NO}$$

This is a reversible reaction, as shown when, by synthetic methods, the components, tropic acid and tropin, are first built up and then readily combine to form atropin and water.

Homatropin hydrobromid, $C_{16}H_{21}NO_3 . HBr$, is the salt of an alkaloid obtained by the condensation of tropin and mandelic acid. It is a white, colorless, odorless, water-soluble powder, used as a rapid and transient mydriatic. It gives Vitali's test.

Physiologic Effects.—Atropin is a depressant of the cerebrospinal nervous system, but a stimulant to the sympathetic. It dilates the pupils, paralyzing ocular accommodation; increases the blood-pressure and the force and frequency of cardiac action; deepens the respiration; flushes the face; diminishes the secretion of sweat, saliva, milk, and bronchial mucus. It is used as an antispasmodic, an anodyne, and an antidote to physostigma and opium. *Dose:* $\frac{1}{100}$ to $\frac{1}{40}$ gr.

A 1 per cent. solution is dropped into the eye to paralyze accommodation and dilate the pupil for eye-testing, and to treat iritis.

Toxicology.—An overdose causes delirium, very rapid pulse, dry throat, thirst, flushed skin like a scarlatinal rash, pupils widely dilated, vision impaired, giddiness, muscular incoördination, retention of urine. In the later stage coma succeeds the noisy delirium, and the respiration becomes slow and shallow, death ending the scene with cardiac or respiratory paralysis.

Treatment.—After washing out the stomach with a solution of tannic acid or evacuation by an emetic, hypodermic injection of strychnin is given to stimulate respiration; of morphin cautiously to allay the cerebral excitement of the first stage. In case of collapse heat is applied to the feet and epigastrium, and tea or whisky administered.

Postmortem appearances are in no way characteristic.

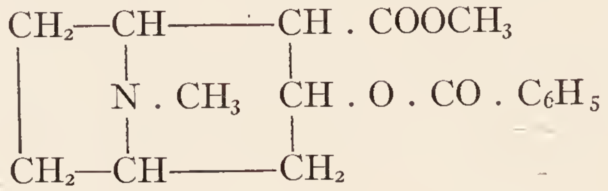
Tests.—*Vitali's.*—A trace of atropin or its salts, moistened with fuming nitric acid and dried on a water-bath, yields a yellow residue (that of morphin would be red), which, moistened with alcoholic potash, gives a violet solution, changing to red.

A few drops of sulphuric acid dissolve a fragment of atropin without change of color; a crystal of potassium dichromate added will, after a while, turn the mixture green, and on warming with a little water develop an odor of orange blossoms.

Physiologic.—Dropped into the eye of a cat, a solution of atropin dilates the pupil widely.

Cocain ($C_{17}H_{21}NO_4$).—Of the several alkaloids of *Erythroxylon coca* this is the only one of importance in medicine. It is obtained in colorless prismatic crystals, which fuse at 98° C. (208.4° F.) and are sparingly soluble in water. It is bitter and later benumbing to the sense of taste. Chemically, it resembles atropin, being strongly alkaline and forming salts, of which the *hydrochlorid* is used extensively in medicine. This is soluble in one-half part of

water, and also in alcohol, glycerin, and chloroform. Heat should not be used in preparing its solutions. The constitution of cocain is shown in the following formula to consist of a 7-carbon ring with a nitrogen bridge. In fact, it is pyrrolidin joined to a piperidin ring:



Boiled with water, it is hydrolyzed into benzoyl-ecgonin, and if acids or alkalis be present, further hydrolysis occurs, with formation of *ecgonin*, benzoic acid, and methyl alcohol:

$$\underset{\text{Cocain.}}{C_{17}H_{21}NO_4} + 2H_2O = \underset{\text{Ecgonin.}}{C_9H_{15}NO_3} + \underset{\text{Benzoic acid.}}{C_6H_5 . COOH} + CH_3OH.$$

This reaction shows that cocain is the methyl ester of benzoyl ecgonin. Locally to mucous membranes, or hypodermically, cocain acts as an anesthetic, rendering minor surgical operations painless. It is given internally to relieve nausea. *Dose:* $\frac{1}{5}$ to $\frac{1}{2}$ gr. (0.015–0.03 gm.). For local application a solution is used, 2 to 10 per cent. Its systemic effect is stimulant and diuretic.

Toxicology.—In overdoses cocain causes nausea, vomiting, vertigo, muscular prostration, and heart failure. Both pulse and breathing are much disordered. At times there is blindness, aphonia, or convulsions.

The habitual use of cocain, or *cocainism*, causes deterioration of the moral sense and varied nervous phenomena.

Treatment.—In treating cocain poisoning, after evacuation of the stomach the chemical antidotes are those used for all alkaloids: tannin and vegetable astringents; iodin, 1 gr., and potassium iodid, 10 gr., dissolved in water. The physiologic antagonists are digitalis and inhalations of amyl nitrite for the syncope; caffein and whisky as stimulants; oxygen for cyanosis; morphin for nervous excitement.

Detection.—(1) Iodin dissolved in potassium iodid solution precipitates cocain red.

(2) Picric acid gives a yellow, powdery precipitate when the cocain is in concentrated solution.

(3) The suspected solution is boiled for a few minutes with sulphuric acid, neutralized with potassium hydroxid, and then treated with a few drops of ferric chlorid. Ferric benzoate is precipitated brownish yellow.

Physiologic Test.—A neutral solution of the cocain hydrochlorid applied, several drops in succession, to tongue or lip causes numbness

and insensibility, lasting a few minutes only. The same effect is obtained on the eye with some transient dilatation of the pupil.

Eucain is an artificial alkaloid, employed locally as a substitute for cocain, because safer. There are two forms, alpha and beta. Alpha-eucain, $C_{19}H_{27}NO_4HCl$, is a benzoyl-methyl-tetra-oxy-piperidin-carboxylic-methyl-ester. Beta-eucain, $C_{17}H_{21}NO_2HCl$, is a benzoyl-vinyl-diaceton-alkamin. A white, neutral, water-soluble powder, less toxic on the heart than cocain or alpha-eucain, and sterilizable without decomposition by boiling. Used in 2 per cent. solution.

Eucain contains a group which is also present in cocain:

$$\begin{array}{c}| \quad\;\; | \quad\;\; | \qquad\qquad\qquad\qquad\quad \\ N—C—C—O\,.\,CO\,.\,C_6H_5 \\ | \quad\;\; | \quad\;\; | \qquad\qquad\qquad\qquad\quad\end{array}$$

Other synthetic preparations, having similar local anesthetic effects, are found to have this same group, probably the cause of this peculiar action. They are:

Stovain, the benzoxy-methyl, dimethyl-amino-butane chlorid. Safer than cocain, it tones the heart and dilates the vessels and is used for intraspinal anesthesia.

Alypin, the chlorid of the benzoyl-ethyl-tetra-methyl-diamido-derivative of secondary propyl alcohol. It is safer than cocain without mydriatic action.

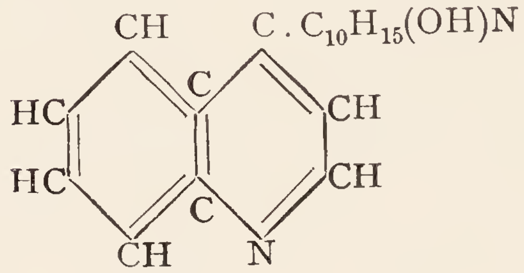
Novocain, the para-amino-benzoyl-diethyl-amino-ethan chlorid, a transient local anesthetic less toxic than cocain or the above substitutes.

QUINOLIN ALKALOIDS

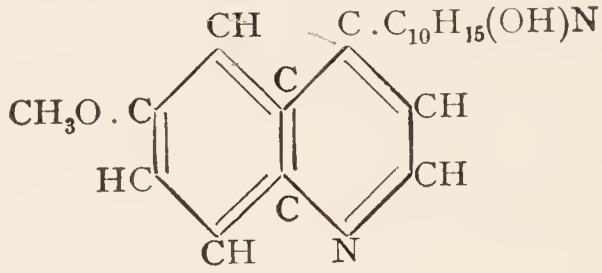
Quinin ($C_{20}H_{24}N_2O_2$).—This and several other allied alkaloids (*cinchonin, quinidin, cinchonidin*) occur in cinchona bark, combined with quinic and quinotannic acids. The best varieties of calisaya contain 4 per cent. of ether-soluble alkaloids, of which 3 per cent. is quinin. The crystalline form contains 3 molecules of water and is with difficulty soluble in water. It is a feeble diacid base, forming hydrogen salts with sulphuric acid—the *sulphate*, $(C_{20}H_{24}N_2O_2)_2H_2SO_4+7H_2O$, and the *bisulphate*, $C_{20}H_{24}N_2O_2 \,.\, H_2SO_4+7H_2O$—both of which crystallize in silky needles, light, bitter, and soluble. The solutions are fluorescent, with a pale-blue color. The bisulphate is by far the more soluble. The sulphate contains 75 per cent. anhydrous quinin and requires 720 parts of water or 86 of alcohol to dissolve it; the bisulphate has 60 per cent. anhydrous quinin and requires for solution only 9 parts of water or 18 of alcohol; the salicylate has 70 per cent. anhydrous quinin and dissolves in 77 parts of water or 11 of alcohol.

It has been established that quinin is a methoxycinchonin and

a derivative of quinolin, because with oxidizing agents it yields quininic acid (methoxyquinolin-γ-carboxylic acid). Both alkaloids contain a group, $C_{10}H_{15}(OH)N$, the structure of which is undetermined. Their constitution, so far as known, is represented by the following formulas, in which it is shown that quinin differs from cinchonin by the substitution of methoxyl, CH_3O for H:



Cinchonin.



Quinin.

In doses of 2 to 5 gr. (0.1–0.3 gm.) quinin acts as a stimulant, especially to the nervous system; in doses of 5 to 30 gr. (0.3–2 gm.) it is an antiperiodic for malarial fevers; in doses of 10 gr. (0.6 gm.), an antipyretic; in doses of 1 to 2 gr. (0.06–0.13 gm.), a general tonic.

In overdoses it produces *quinin fever*, with erythema, ringing in the ears, hemorrhage into the labyrinth, with deafness, transient blindness, destruction of the blood-corpuscles, and even respiratory failure.

Tests.—(1) A salt of quinin with chlorin or bromin water treated with excess of ammonium hydroxid gives a characteristic emerald-green color, due to *thalleioquin*.

(2) Dilute solutions of quinin salts acidulated with sulphuric acid give a beautiful light blue fluorescence. A red color with concentrated sulphuric acid shows that other substances are present.

Cinchonin, $C_{19}H_{22}N_2O$, is found with quinin in almost all the cinchona barks. It is a white, bitter, crystalline alkaloid, resembling quinin in ordinary properties, though medicinally much less effective. It is a quinolin derivative, as stated above.

The *doses* of the cinchonin salts are about double those of the quinin salts.

Tests.—(1) A salt of cinchonin with chlorin or bromin water yields a yellowish white precipitate insoluble in ammonia.

(2) A neutral solution of cinchonin gives with potassium ferrocyanid a white precipitate soluble in excess. This solution in excess, treated with an acid, yields a golden yellow precipitate.

Strychnin ($C_{21}H_{22}N_2O_2$).—This alkaloid, accompanied by *brucin*, is contained in the seeds of *Strychnos nux vomica* and different plants of the same genus. They are usually extracted from *nux vomica*, which contains from 3 to 4 per cent. of alkaloids.

Properties.—Strychnin crystallizes in white, rhombic prisms, without odor, but with an intensely bitter taste. It is very sparingly soluble in water, but sufficiently so to impart a bitter taste even when the amount is only 1 : 700,000. It is more soluble in acidulated water and in chloroform.

Both strychnin and brucin are strong monacid bases, forming salts, many of which are soluble in water. An official salt is the *sulphate*, $(C_{21}H_{22}N_2O_2)_2H_2SO_4, 5H_2O$. This crystallizes in rectangular prisms, is soluble in water and alcohol, and is intensely bitter.

While little is known of the constitution of strychnin, it is considered to be a tertiary base, and as quinolin is a product of its distillation with potash, it is probably a derivative of quinolin.

Medical Uses.—Strychnin is a bitter tonic, stimulating reflex activity, and in large doses causing tetanic convulsions. It augments the force of the heart's action, raises blood-pressure, increases the depth and frequency of respiration. *Dose* of strychnin or its salts: $\frac{1}{60}$ to $\frac{1}{12}$ gr. (0.001–0.005 gm.).

Toxicology.—*Poisonous Symptoms.*—The most marked effects are the convulsions, which at first are *clonic* (intermittent), but as the intervals become shorter and the paroxysms longer eventually become *tonic* (tetanic). The mouth is drawn in the *risus sardonicus*, and the body usually bent back so as to rest on the heels and occiput (*opisthotonos*). The spasms of the diaphragm, drawing upon the ensiform cartilage, cause epigastric pains. The contractions of the respiratory muscles produce a sense of suffocation which may end in asphyxia. The mind remains clear to the last; the pupils contract during the paroxysm. The reflex excitability is so great that a loud noise or the touch of a medicine glass to the lips brings on a convulsion. Vomiting is readily induced and persists when once excited.

Should a paroxysm last too long, asphyxia may prove fatal. Many repetitions of the painful spasms may cause death in the intervals, as the result of exhaustion.

Fatal Period.—As a rule, the symptoms appear in less than twenty minutes after administration, but may be delayed for an hour. Usually, if the dose be very large, death occurs within two hours, sometimes in a few minutes. There are cases of death occurring as long as six hours after taking the poison.

Fatal Dose.—The smallest amount known to have caused death is $\frac{1}{4}$ gr. On the other hand, a dose of 20 gr. has been taken and did not prove fatal.

Treatment.—After the inhalation of chloroform to control the spasms, the stomach tube may be introduced, and protected by a wooden wedge between the teeth. Warm water containing potassium permanganate, 4 gr. in 11 fl. oz., should be used freely to

wash out the stomach. In the absence of a tube, emetics of mustard or zinc sulphate should be given, or hypodermics of apomorphin. Chloral hydrate in 30-grain doses should be given by the rectum, and retention insured by giving chloroform or amyl nitrite inhalation. Gentle narcosis and perfect quiet are desirable.

Detection.—(1) If strychnin be present in amounts to be recognized by chemical tests, a bitter taste will be perceptible. If this taste be absent, no other tests will show strychnin.

(2) A small quantity on a white dish dissolves in a little concentrated sulphuric acid without color.

(3) A small portion of powdered potassium dichromate dusted over the above solution in sulphuric acid produces a transient blue, then an intense violet color, which gradually changes to bright red, then to rose pink, and lastly to yellow. This reaction is sufficiently delicate to reveal 1 : 50,000.

Fallacy.—A mixture of morphin or heroin with 10 per cent. of hydrastin gives with this test a similar play of colors.

(4) *Sonnenschein's reagent,* cerosoceric oxid, is first made by heating cerium oxalate to redness and then dissolving it in 30 parts of sulphuric acid. A fragment of strychnin stirred into a drop of this solution causes a play of colors—blue, violet, and red.

Physiologic Test.—When a small frog is immersed in a solution of strychnin, or when a hypodermic injection of it is given to frogs or white mice two weeks old, muscular twitchings and convulsions are produced, ending in tetanic rigidity and death.

Brucin ($C_{23}H_{26}N_2O_4, 4H_2O$).—This alkaloid is found with strychnin. It is obtained in colorless prismatic crystals, slightly more soluble in water and alcohol than strychnin, readily soluble in chloroform and amyl alcohol. It resembles strychnin in being intensely bitter, a strong monacid base, and a spinant poison, though its physiologic energy is only one twenty-fourth of that of strychnin. It is a tertiary base, forming salts which are soluble and crystalline.

Medical Uses.—It is a bitter tonic. *Dose:* 0.08 to 0.5 gr. (0.005–0.03 gm.).

Tests.—(1) A solution of brucin treated with nitric acid gives a solution having a deep red color, which when warmed turns yellow. If a reducing agent be added, such as a crystal of stannous chlorid or of sodium thiosulphate, the color changes to an intense violet.

(2) A concentrated brucin solution treated cautiously with drops of chlorin water gives a bright red color, changing to violet. Excess of chlorin water decolorizes it, and ammonia turns it brown.

PHENANTHRENE ALKALOIDS

When the unripe heads of certain kinds of poppy (*Papaver somniferum*) are incised, a juice exudes and dries to a brown paste, called *opium*. Opium contains at least seventeen different alkaloids, of which the most important is *morphin*. Others worthy of mention are *codein*, *narcotin*, *thebain*, and *papaverin*. They all exist in combination, partly with sulphuric acid, but mainly with *meconic acid*. This is a hydroxydicarboxylic acid of the fatty series, having the formula $C_5HO_2(OH)(COOH)_2$. It can be obtained as crystals, and is detected by the intense dark-red color given with neutral ferric chlorid, the color persisting after treatment with mercuric chlorid or boiling with hydrochloric acid.

Opium occurs in masses or powder of a chestnut brown color, a narcotic odor, and a bitter taste. The crude drug should contain not less than 9 per cent. of morphin, and dry powdered opium not less than 12 per cent. Morphin is the active narcotic principle in all the official preparations of opium and in various proprietary anodynes and carminatives, such as *Mrs. Winslow's*, *Dalby's*, *Battle's*, also in *nepenthe*, *chlorodyn*, and most *opium cures*.

The *dose* of powdered opium of standard morphin strength required to narcotize is 5.6 times as much as that of morphin sulphate.

Morphin ($C_{17}H_{19}NO_3$).—The free base takes 1 molecule of water of crystallization to form colorless prisms. Slightly soluble in water and cold alcohol, it dissolves easily in potash and soda, to be precipitated again on the addition of an acid. This behavior is due to the presence of phenolic hydroxyl, which group is the cause of the blue color reaction with ferric chlorid. It contains another hydroxyl group which is alcoholic. Morphin boiled with zinc dust yields pyridin, quinolin, phenanthrene, and other substances showing it to be a polynucleated compound. When one of its hydrogen atoms is replaced by methyl, the product is codein. *Codein* is soluble in water, alcohol, and ether, and readily forms salts with acids. As a hypnotic the dose is twice as large as that of morphin, being $\frac{1}{2}$–1 gr. (0.03–0.13 gm.).

Dionin is dimethyl morphin hydrochlorid, and like codein.

Heroin, used as a substitute for codein, is diacetyl morphin, or the acetic ester of that alkaloid. Used for coughs, *dose:* $\frac{1}{20}$–$\frac{1}{6}$ gr. (0.01 gm.).

Apomorphin, $C_{17}H_{17}NO_2$, is prepared by heating morphin with hydrochloric acid in a sealed tube to 140° C. (252° F.) for three hours. The chlorid occurs in colorless crystals turning greenish by exposure to light. Soluble in 7 parts of water, it is used hypodermically as an emetic in five drops of a 2 per cent. solution.

Morphin is a monacid base, forming well-defined salts with

the acids. While the hydrochlorate and acetate are official, the salt commonly used is the *sulphate*, $(C_{17}H_{19}NO_3)_2H_2SO_4, 5H_2O$.

Morphin sulphate is dispensed in white, snowy needles, odorless and bitter. It is readily soluble in water and moderately so in alcohol, giving a neutral reaction. *Dose:* $\frac{1}{8}$ to $\frac{1}{2}$ gr. (0.008–0.03 gm.). One-sixth of a grain is equal in anodyne and narcotic properties to 1 gr. of opium. Cases of intense pain usually require several doses of $\frac{1}{4}$ gr. hypodermically.

Toxicology.—*Symptoms.*—The poisonous effects of a dose by the mouth begin to show in about twenty minutes. A hypodermic dose causes drowsiness earlier and some relief of pain in five minutes. There is an initial stage of exhilaration with strengthening of the pulse. This soon ends in giddiness, languor, somnolency, nausea, itching of the skin, and slow, full pulse. The pupils are contracted to the size of a pin's head, and are not influenced by light and darkness. There are shallow and stertorous respirations, with peculiar death-like pauses lasting half a minute, alternating with periods of about thirty irregular respirations.

The breathing may not have this rhythmic character, but may pass gradually and calmly to feeble and slow breathing, asphyxia, and death. As the respiration is disturbed, the surface grows blue, cold, and damp; the urine is retained. As death approaches, the coma is profound, the pulse becomes weak, and the pupils may dilate.

Anomalous cases are reported in which convulsions occur; spontaneous vomiting and diarrhea have been known to eject the poison and save the patient. Very rarely the pupils have not been contracted. *Relapse* into coma and death has happened even after the patient has recovered consciousness.

Fatal Period.—Death has occurred in forty-five minutes, and, on the other hand, has supervened after the lapse of four days. In most of the fatal cases life is prolonged from six to twelve hours. If breathing can be kept up for forty-eight hours, recovery is highly probable.

Fatal Dose.—Most persons not habituated to opium would die after 5 to 10 gr. of opium or 1 to 2 gr. of morphin. There are persons highly susceptible who are poisoned by doses of less than 1 gr. of morphin; while, on the other hand, there are those habituated to the use of opium who not only survive enormous amounts, but take daily doses ten times the fatal quantity without apparent injury.

Treatment.—The stomach should be washed out with the siphon tube, using water containing potassium permanganate, 10 gr. to the tumblerful. This agent promotes morphin oxidation. If this

be not procurable, the washing may be done with infusions of tea or tannic acid, or mixtures of powdered animal charcoal and water. Emetics of mustard may be given in 1 or 2 doses of a teaspoonful each, or zinc sulphate, 20 to 30 gr. A prompt emetic given hypodermically is apomorphin, 5 to 10 min. of a 2 per cent. solution. When the permanganate is given subcutaneously, it forms with the serum of the blood an albumin manganic oxid which has the power of decomposing the morphin. Solutions of 0.5 per cent. strength (1 gr. in 2 fl. oz.) may be injected in amounts of 1 to 6 fl. dr. at two or three points.

The symptoms to be combated are failure of respiration at first, and later on the weakened action of the heart. Somnolency itself is not important if the patient's breathing be sustained. In time the poison will be oxidized or eliminated. To stimulate respiration it may be necessary to make the patient conscious of his needs by shouting in his ear, by shaking, flogging with a wet towel, applying electricity to the cutaneous surface intermittently, or by moderate walking. A good rate of respiration must be kept up even if resort must be had to the method of artificial movements of the arms. Of use may be found hypodermic doses of strychnin, $\frac{1}{20}$ gr., cocain hydrochlorate, $\frac{1}{4}$ gr., or atropin sulphate, $\frac{1}{60}$ gr. To stimulate the heart in the later stages, coffee and brandy are indicated.

Postmortem Appearances.—The autopsy does not reveal any local action on the mucous membranes of the alimentary tract. Neither can any characteristic lesion be discovered elsewhere. Generally there are found fulness of the cerebral vessels, meningeal effusions, and congestion of the lungs.

Tests.—Many of the tests are based upon the readiness with which morphin is oxidized and the colored products obtained by different degrees of oxidation. These are pseudomorphin and compounds of morpholin and phenanthrene.

Lefort's Iodic Acid.—Upon a fragment of the morphin on a dry white dish is placed a drop of a solution of iodic acid, and the dish is then set aside for ten minutes. If the brown color of free iodin appear, the spot is dried and, with chloroform, the iodin is washed off until no color remains. (The chloroform residue will turn blue with starch.) After drying the washed spot it is wet with a drop of 10 per cent. ammonia water, which, reacting with morphin oxidation products, gives a mahogany color.

DELICACY.—A definite reaction is obtained with $\frac{1}{6400}$ gr.

Ferric Chlorid.—A fragment of the solid or the residue suspected is moistened on a white dish with neutral ferric chlorid solution. A blue color appears, which may be greenish if excess of ferric chlorid has been used, destroyed by alcohol. The color

is probably due to a phenol compound of a ferrous base. This reaction is given with many aromatic compounds containing the phenolic hydroxyl, but no other ordinary alkaloid gives it. The morphin blue is changed to orange and yellow by *nitric acid.*

Fröhde's Molybdic Acid.—The reagent is a freshly made solution of 1 or 2 mg. of molybdic acid or ammonium molybdate in 1 c.c. of sulphuric acid. The dried material on a white dish is treated with 1 drop of the reagent. A purple color, changing to violet and green, indicates morphin. As other alkaloids give bluish and greenish colorations with this reagent, it is advisable to identify the color by a control test on a fragment known to be morphin.

DELICACY.—A decisive reaction is given by $\frac{1}{6400}$ gr.

Sulphuric and Nitric Acids.—A trace of morphin on a white dish is touched with a drop of concentrated sulphuric acid; a colorless solution is formed. After standing for fifteen hours this solution is treated with a trace of nitric acid, which gives a bluish-violet color, changing to blood red.

DELICACY.—This reaction is decided with 0.01 mg. of morphin.

ALKALOIDS OF UNKNOWN CONSTITUTION

Veratrin.—This name, according to the U. S. Pharmacopeia, covers a mixture of alkaloids obtained from the seed of *Asagræa officinalis.* It is a white, inodorous powder, soluble in water and alcohol. An important part of this mixture is the alkaloid *cevadin* or *crystallized veratrin* ($C_{32}H_{49}NO_9$). Another alkaloid present is *jervin* ($C_{26}H_{37}NO_3$), with traces of *amorphous veratrin.* Like the aconite alkaloids, these are quinolin derivatives.

Dose of fluidextract of veratrum viride (American hellebore): 1 to 3 min. (0.06–0.18 c.c.). It is a powerful cardiac depressant.

Toxicology.—*Symptoms.*—Poisonous doses of veratrum viride or veratrin cause nausea, vomiting, abdominal pain, weakness, feeble pulse, giddiness, loss of sight, dilated pupils, drowsiness, coma, with death from asphyxia.

Fatal Dose.—The fluidextract has been fatal in doses of 70 min. (4.3 c.c.).

Treatment.—The stomach should be thoroughly washed out by the siphon tube, or emetics employed. Tannic acid or vegetable astringents will precipitate the alkaloid. Cardiac depression may be combated with atropin or strychnin, or brandy hypodermically. The posture should be recumbent, and artificial respiration used if necessary.

Tests.—(1) Veratrin (U. S. P.) in dry fragments on a white plate dissolves yellow in concentrated sulphuric acid. On standing the yellow solution changes to bright red, and later on to a darker red or crimson, which persists for hours.

(2) Veratrin dissolves in hydrochloric acid and on boiling develops a persistent bright red color.

(3) One part of veratrin rubbed with 6 parts of cane-sugar is treated with a few drops of strong sulphuric acid. The color developed is yellow, then green, and finally blue.

(4) *Physiologic Test.*—The ptomains which give color products like those described above do not have the same effects on a live frog. Hypodermic injection of veratrin causes vomiting, slow pulse, convulsions, and death.

Gelsemin is a poisonous alkaloid of *Gelsemium sempervirens*, the yellow jessamine or jasmine. It is a white, very bitter, inodorous powder, used in medicine as a nervous and arterial sedative. In overdoses it is a violent poison. The fluidextract of the root is given in doses of 2 to 10 min. (0.12–0.65 c.c.). The dose of the alkaloid is $\frac{1}{60}$ to $\frac{1}{30}$ gr. (0.001–0.002 gm.).

Gelseminin is a brownish alkaloid separable from the same plant.

Toxicology.—*Symptoms.*—The poisonous effects are shown by falling of the eyelids, double vision, dilated pupils, great muscular weakness, depression of the temperature, pulse, and respiration. Death is by asphyxia, the mind remaining clear.

Fatal Dose.—Three teaspoonfuls of the fluidextract have caused death. The symptoms appear promptly, and death may follow in an hour or be delayed eight hours.

Treatment.—After the stomach has been thoroughly washed out stimulants are given, and hot applications made to the epigastrium and extremities. Digitalis will strengthen the heart and atropin the respiration.

Tests.—The alkaloids, when touched with concentrated alcohol on a white plate, yield a yellow-brown color. A fragment of potassium chromate or cerosoceric oxid changes the color to red and purple, the final color being green.

Physiologic Test.—Administered hypodermically to frogs, cats, or rabbits, the alkaloids cause prostration, convulsions, dilated pupils, and asphyxia.

PTOMAINS

Not infrequently cases of poisoning occur from eating foods of animal origin—such as meats, fish, cheese, milk, custards—that have become unwholesome from the products of bacterial growth. These products are considered as belonging to one of the two classes, ptomains and protein toxins. *Leukomains* constitute a class of substances, such as the purin bases and creatins, some of which are poisonous, and all of which are produced by the normal breaking down of tissue in the living body, or, in other

words, the splitting of protein by enzyms secreted by the body cells. *Auto-intoxication*, or self-poisoning, such as "biliousness" and uremia, is the result either of the internal formation of ptomains or of the undue accumulation of leukomains in the body. The leukomains, when not duly oxidized to urea, CO_2 and H_2O, often cause serious disturbance of health, and the ptomains and toxins are sometimes highly toxic. If the phosphorized fat, *lecithin*, be acted on by putrefactive bacteria, cholin may be split off as a ptomain. If the same cleavage be done during life by the body cells, the cholin is a leukomain, and if not normally oxidized, causes auto-intoxication.

Ptomains are soluble basic bodies formed by the action of certain micro-organisms on putrefying protein material. The amino-acids ornithin and lysin, constituents of pure proteins, subjected to bacterial action, split off CO_2 and change to putrescin and cadaverin (p. 506). Some of them are active poisons, but others, like the methylamins and ethylamins, are harmless. They are alkali-like in some respects, and hence were formerly termed *cadaveric alkaloids*. They are strongly basic and combine with acids to form salts. Like the proteins from which they are derived, they are precipitated with the chlorids of mercury, gold, and platinum; with picric acid, tannic acid, phosphomolybdic acid, and phosphotungstic acid. Having these reactions in common with vegetable alkaloids, they may be considered as related to them. However, many of them differ from true alkaloids in constitution, having their nitrogen in an open-chain molecule of the fatty series, and belonging to the class of amins (p. 503). These ptomains, which do not contain a closed chain (acyclic), are subdivided into those free from oxygen and those containing that element. The acyclic free from oxygen comprise the methylamins, butylamin, amylamin, neuridin, saprin, cadaverin, putrescin, spermin, mydalein. The acyclic ptomains containing oxygen include cholin, neurin, muscarin, betain, gadinin, mytilotoxin, and a few others.

In the following list are included the ptomains which have the nitrogen in a closed chain (pyridin ring) like true alkaloids (cyclic), and those as yet unclassified: collidin, parvolin, corindin, morrhuin, asellin, typhotoxin, tetanin, spasmotoxin, tetanotoxin, pyocyanin, tyrotoxicon.

Of the above list, a small number of ptomains are known to be injurious in foods. These are tyrotoxicon of milk, cream puffs, ice cream, and cheese; mytilotoxin of mussels and oysters; muscarin of mushrooms and meat; and from spoiled fish and meat, cholin, neuridin, neurin, cadaverin, putrescin. While they are decomposition products of protein, apparently they may be engendered in tissues still living, such as fresh oysters and mussels. To pro-

duce them is required a certain favorable combination of special micro-organisms, protein, air, and temperature. They are unstable, changing in a short while through many stages. In most cases decomposition has not gone far enough to make the food offensive. The toxicity may be great when there is no taint perceptible to smell or taste.

Symptoms.—These make their onset soon after eating the poisoned food. They may be described broadly as the symptoms of gastro-enteritis, with depression and other nervous disturbances. There are in most cases marked thirst, salivation, nausea, vomiting, abdominal pain, diarrhea, cramps in the legs, great prostration, chills, feeble pulse, dilated pupils, drowsiness or delirium, numbness, paralysis, exhaustion, and collapse.

Sometimes the postmortem reveals inflammation of the stomach and bowels, though fatal cases occur which are free from morbid changes in the anatomy of the digestive tract.

Cholin ($C_5H_{15}NO_2$) (*bilineurin*) is a complex amin occurring in the bile of animals, in the human placenta, in the yolks of eggs, in hops, and in fungi.

Cholin is formed by treating an aqueous solution of trimethylamin with ethylene chlorhydrin:

$$N(CH_3)_3 + C_2H_4ClOH + H_2O = \underset{\text{Cholin.}}{C_2H_4OHN(CH_3)_3OH} + HCl.$$

The lecithins of the animal corpse produce cholin during the first forty-eight hours of putrefaction. On and after the third day cholin diminishes, while other closely related bodies, such as neuridin, putrescin, and cadaverin (*ptomains*), appear and increase daily. *Muscarin* can be made by oxidizing cholin with nitric acid. The effect of heat is to split cholin into glycol and trimethylamin.

Properties.—It is a syrupy fluid, soluble in water and alcohol, and strongly alkaline. It absorbs carbon dioxid from the air like other strong bases, and forms a hydrochlorid which crystallizes in plates like cholesterin. In large doses its action is poisonous.

Lecithin is a complex body commonly found in yolk of egg, brain and nerve tissue, blood, pus, milk, etc. The several varieties are compounds of cholin and glycerophosphoric acid with the acids of fat. This composition is shown by the following formula which gives glyceryl united to two stearic acid groups and one of phosphoric acid, linking the cholin:

$$C_3H_5\begin{cases} O\,.\,C_{18}H_{35}O \\ O\,.\,C_{18}H_{35}O \qquad /\!/(CH_3)_3 \\ O\,.\,PO_3H\,.\,C_2H_4N-OH. \end{cases}$$

With alkalis they saponify, yielding the fatty acids, the glycerophosphoric acid, and cholin. Like the true fats, they are soluble in ether.

Neurin, $C_5H_{13}NO$, is an amin derivative occurring as a product of decomposition in the tissues of the brain and suprarenal capsule. It is one of the ptomains of muscular tissue. It can be formed by boiling cholin with baryta water and thereby abstracting the elements of water:

$$\underset{\text{Neurin.}}{C_2H_3OHN(CH_3)_3} + H_2O = \underset{\text{Cholin.}}{C_2H_4OHN(CH_3)_3OH}$$

It is a poison much more powerful than cholin, the symptoms resembling those of obstruction of the bowel, with nausea, pain, and depression.

Diamins.—This class of compounds, containing two NH_2 groups, has several representatives, basic in character, among the putrid products, viz.: *trimethylenediamin*, $H_2N \cdot (CH_2)_3NH_2$, found in the cultures of comma bacillus; *tetramethylenediamin*, or *putrescin*, $H_2N \cdot (CH_2)_4NH_2$, found in cultures of comma bacillus and putrid flesh; *pentamethylenediamin* or *cadaverin*, $H_2N \cdot (CH_2)_5NH_2$, occurring in the later stages of putrefaction, after cholin has disappeared, as a basic liquid with a disagreeable odor; *neuridin*, isomeric with cadaverin, and produced with cholin as an early putrid product; *mydalein*, a diamin of unknown structure, product of putrefaction, actively poisonous, causing dilated pupils, diarrhea, convulsions, and paralysis (p. 506).

Amanitin ($CH_3 \cdot CHOH \cdot N \cdot OH \cdot (CH_3)_3$) (*isocholin*) occurs as an alkaloid in the red, fleshy mushroom, *Agaricus muscarius*, or *fly agaric*, which is poisonous to flies and man. It is isomeric with cholin, and can be prepared by introducing methyl into aldehyd ammonia. Nitric acid oxidizes it to *muscarin*.

Muscarin, $CH_2CH(OH)_2OHN \cdot (CH_3)_3$, is found in the mushroom, *Agaricus muscarius*, and is also a ptomain. Chemically, it is related to amanitin, neurin, and cholin, and can be produced synthetically from the latter.

Properties.—When dry, it occurs in odorless and tasteless, irregular crystals, which deliquesce to form a syrupy liquid, strongly alkaline, soluble in water and in alcohol, insoluble in chloroform and in ether. It can be reduced to cholin and oxidized to betain. It breaks up into trimethylamin. Precipitated by excess of platinum chlorid, it forms octahedral crystals, while the chlorplatinate of cholin crystallizes in plates.

Toxicology.—*Symptoms.*—Muscarin is far more poisonous than cholin or neurin, and is the active cause of the symptoms of mush-

room poisoning. These are vomiting, griping pains in the stomach and intestine, slow pulse, ending in arrest of the heart's action; contraction of the pupils, salivation, and fatal collapse. Alarming symptoms may follow $\frac{1}{50}$ gr. (1 mg.).

Treatment.—Its physiologic antagonist and antidote is atropin. Stimulants, morphin, and strychnin are also of service.

TOXINS

Toxins are poisonous bases produced in the animal body by certain bacteria, which also cause infectious diseases. Such are diphtheria toxin, typhotoxin of typhoid fever, tetanin, and spasmotoxin of tetanus.

Food Toxins.—The protein toxins that cause food poisoning are either—(1) the poisonous products of specific bacteria, not putrefactive, growing in the meat after slaughter; or (2) they are products of specific bacteria infecting the tissues of the food animals before slaughter.

(1) A common form is *botulism* or sausage poisoning, caused by the *Bacillus botulinus* contaminating ham, sausage, and fish. Other powerful toxins have been developed by certain species of bacteria, like *Proteus vulgaris*, B. enteritidis, B. suipestifer, and B. paratyphosus, growing in pork and beef sausages. If a pickling solution of 16 per cent. of sodium chlorid be used B. Botulinus does not develop, and if the food be thoroughly cooked both the bacilli and the toxins are destroyed. Sausage poisoning manifests itself usually within twenty-four hours, sometimes as soon as half an hour, though the onset may be delayed for a week.

The *symptoms of sausage poisoning* are epigastric discomfort, belching, nausea, vomiting, gripes, diarrhea, followed by constipation. After a few days the nervous symptoms appear: dilated pupils, blindness, falling of the lids, paralysis of the tongue and pharynx, and loss of voice. The secretions may be suppressed, the pulse irregular, and the muscles weak to exhaustion. In a few cases there are somnolence, giddiness, convulsions, paralysis, and possibly acute nephritis. Death may follow delirium and coma, or a favorable turn may lead to slow recovery after many days.

The *postmortem appearances* have been in the nature of hyperemia of meninges, lungs, spleen, kidneys, liver, and alimentary tract. Nothing has been found characteristic of *botulism*.

(2) The toxins of the other class result from the activities of the pathogenic bacteria before the animals are killed. The meat from cows and calves that have had pyemia, septicemia, or specific enteritis will cause symptoms something like arsenic poisoning,

cholera, or typhoid fever. These are headache, vomiting, profuse diarrhea, gripes, chills, and fever.

Treatment.—The efforts of nature to remove the poison should be promoted by free potations of warm water and salt, followed by mild laxatives and high irrigation of the intestines with enemas. Excessive vomiting, purging, and pain are to be relieved by hypodermic injections of morphin. Stimulants are needed, and subcutaneous injections of normal salt solution will be helpful.

Resemblances Between Ptomains, Toxins, and Vegetable Alkaloids.—A study of the symptoms narrated above shows certain points of resemblance to the symptoms caused by alkaloidal poisons. For example: somnolency may be mistaken for the effects of morphin; dilated pupils and delirium are prominent signs of poisoning from plants yielding atropin; paralysis, numbness, convulsions, and stupor may be found after doses of conium and gelsemium.

The chemical tests dependent on color changes due to oxidizing agents, when applied to vegetable alkaloids, give results closely resembling those caused in certain ptomains, so that mistakes have occurred in the work of expert chemists. The symptoms of the case, the physiologic tests on lower animals, and all known chemical tests must be studied and harmonized before the analyst can be certain that he is not dealing with ptomains, but that he has detected morphin, atropin, coniin, nicotin, strychnin, veratrin, or colchicin.

The various methods employed for separation of the alkaloids are none of them perfectly successful in excluding the ptomains. Perhaps the best yet devised is that known as the—

Kippenberger Process.—Separation is accomplished by virtue of the mixture of tannic acid and glycerin, which dissolves the vegetable alkaloids, but leaves ptomains and toxalbumins undissolved. The alkaloids are separated from one another by shaking the liquid with successive immiscible solvents in a separating funnel with a stopcock (Fig. 83). Each solvent extracts a group, which is left on evaporation of the solvent, and the alkaloid is detected in the residue by appropriate tests.

The material, finely minced, is macerated at 40° C. (104° F.) in a 10 per cent. solution of tannic acid in glycerin for two days. It is then put in a bag of straining cloth and the fluid part pressed out. This fluid part is heated to between 60° C. (140° F.) and 70° C. (158° F.) for two hours; cooled and filtered. The filtrate is shaken with *petroleum ether*, which separates the fats. Any petroleum ether not separated from the liquid is removed by evaporation on a water-bath, and the liquid is now shaken with *chloroform* while still acid. This chloroform-acid extract removes aconitin, cantharidin, colchicin, digitalin, jervin, narcotin, picrotoxin, and traces

of strychnin, veratrin, brucin, delphinin, and narcein. The liquid, made alkaline with potassium hydroxid, is again shaken with another portion of chloroform, which now removes apomorphin, atropin, brucin, codein, coniin, emetin, nicotin, pilocarpin, spartein, strychnin, veratrin. Potassium bicarbonate is now added to change any excess of hydroxid to carbonate, and the mixture shaken with chloroform containing 10 per cent. of alcohol, which extracts morphin and narcein. The liquid is lastly saturated with sodium chlorid and shaken with chloroform containing 15 per cent. of ether, which removes strophanthin.

Infection Toxins.—In the cells of bacteria are built up poisonous substances which may be retained or may pass out by diffusion. The filtrate of a culture of diphtheric bacilli is poisonous because of the soluble toxin excreted by the bacilli. In a few days *toxemia* is produced by absorption of toxins from the diphtheric membrane in the throat.

The filtrate of a typhoid culture is harmless because the toxin has been retained by the typhoid bacillus. But if the precipitated bacilli be dried, pulverized, and suspended in water, the intracellular toxin is liberated and the mixture is poisonous. In the period of invasion of typhoid fever the bacilli find access to the circulation and multiply there. As they die from day to day, their intracellular toxins are set free and cause the fever of a septicemia or bacteremia until the bacilli are all gone.

Antitoxins.—When the body is infected by a toxin a defensive protein of unknown composition is formed in the blood, which combines with and neutralizes the toxin. The antitoxin of diphtheria is produced artificially by injecting horses with a culture of the diphtheria bacilli. By gradually increasing doses the animal acquires *immunity*, and its serum, drawn from the vessels, is so rich in the antitoxin that when injected into man it gives immunity from or cures the infection of diphtheria.

Agglutinins, Precipitins, and Lysins.—When the body is injected with certain bacteria or cells, called *antigens*, *antibodies* are developed in the blood. These bodies cause a reaction when they are mixed with the special injected material.

Agglutinins.—The blood-serum of a case of infectious disease contains *agglutinin*, which has the property of clumping together the specific bacteria in a culture. Thus, in *Widal's test* for typhoid fever, blood from the patient is added to a fresh culture of typhoid bacilli, and if the case be typhoid fever, the bacilli adhere in tangled masses. They are not killed, but held in check, so that they do not multiply and are more easily exterminated.

A **precipitin** is an antibody which acts as a protective against foreign proteins in the blood. It confers upon the serum the

special property of precipitating from solution the protein that excited its production.

Lysins are cell-destroying substances developed in the serum by the injection of non-fatal doses of bacteria or their products. *Bacteriolysins* are bacteria-destroying, soluble proteins of the blood plasma. *Hemolysins* are able to destroy the red blood-cells of another species of animal. An *autolysin* destroys cells in the animal's own body; a *homolysin*, those in an animal of the same species; a *heterolysin*, those in an animal of different species. These lysins consist of two substances called the *immune body* and the *complement*. The lysins cannot act upon their objects of attack without an intermediate substance. This substance, the *immune body*, has two chemical affinities: (1) It is specific for each lysin that is developed, and (2) it acts by uniting with the bacterial product on the one hand and the blood *complement* on the other.

The fixation of the complement is the basis for *Wassermann's test* for syphilis. Some blood-serum of the suspected patient, and alcoholic extract from a syphilitic liver or lipoids from heart and spleen of animals (antigen) are mixed with fresh guinea-pig serum (complement) and incubated one hour. Then this is added to a mixture of red blood-cells of another animal with the serum of a rabbit which has been immunized to them (hemolysin). After incubating one hour, if the blood-cells are not dissolved it shows that the complement is fixed and the patient is syphilitic.

Opsonins (*caterers*) are certain elements of blood-serum, different from lysins and antitoxins, which unite chemically with invading bacteria and alter them so that the leukocytes can phagocyte and destroy them. Each variety of disease germ has its corresponding opsonin. The amount of opsonins in the blood of an individual determines his susceptibility to bacterial invasion. To measure this resistance of the patient, as compared with that of a healthy person, is to find out his "opsonic index."

To do this, cultures are made of a mixture of the serum of the patient's blood with washed leukocytes and emulsion of the specific bacteria. At the same time a control experiment is made with normal blood-serum. The average of germs to leukocytes is counted and compared in the two experiments. The result is stated as high, normal, or low opsonic index. Cases of bacterial infection with normal or low index are treated by inoculating the patient with a vaccine of the specific bacteria, watching the opsonic index. By this means it is intended to stimulate the tissues to an increased production of opsonins until the level is maintained higher than normal and the invading bacteria are disposed of.

PROTEINS OR ALBUMINOUS MATTER

The compounds considered under this head are the post-mortem representatives of the protoplasm which constitutes the indispensable basis of life in plants and animals. The animal body is especially rich in these proteins or albuminous substances, as they are sometimes called. Apparently, they are all formed originally by plants only. Animals take the fundamental structure in vegetable food and afterward make some changes in them, but do not make them by synthesis of their elements.

They belong to the class of *colloids*, as most of them do not crystallize nor diffuse through the membrane of a dialyzer without difficulty, owing to the large size of the molecule. They are non-volatile; without odor or taste; some are soluble in water, others are insoluble; all of them are optically active, turning the polarized ray to the left. All of them contain carbon, hydrogen, oxygen, nitrogen, and traces of mineral salts. Other constituents found in some of them are sulphur, phosphorus, and iron.

It is not known if their constitution be definite; it is certainly very complex. The great number and variety of proteins in plants and animals is explained by the fact that many of them contain as many as 100 asymmetric carbon atoms (p. 426), thus permitting special isomerids, enormous in number, and possible modifications of properties to an unlimited extent. These differences in spatial arrangement of the atoms are frequently of greater importance for the direction of vital processes than coarser differences in chemical structure.

By blending certain amino-acids Fischer has succeeded in producing artificially *polypeptid* bodies having some resemblance to peptones in properties and reactions, but no structural formula can be made to represent pure protein. Ignorance of their true constitution is the excuse for a classification less accurate than is desirable, based upon their differences in behavior when heated, when treated with acids and alkalis, and when *salted out*. Some of them exist already formed in the animal tissues and fluids, and are sometimes referred to as *native proteins* (albumins, globulins, nucleo-albumins). Others are products of the action of heat and chemicals or of enzyms upon the native proteins, and hence are referred to as *derived proteins* (albuminates, proteoses, peptones).

The *simple proteins*, albumin and globulin, are present in all the fluids and solids of the body except the tears and sweat. Their molecular weights have been estimated as about 10,000, and while the molecules must be variable in size, all are very large, their percentage composition averaging as follows: carbon, 52; hydrogen, 7; nitrogen, 16; oxygen, 22; sulphur, 1; phosphorus, 0.5.

Decompositions.—By the action of hydrochloric acid the nitrogen of the proteins is divided among three fractions of the molecule: *ammonia*, *amino-acids*, and *diamino-acids*. Alkalis have the property of separating a portion of the nitrogen as *ammonia*. If the proteins be boiled with caustic alkalis, only a part of the sulphur goes off in a sulphid combination, the remainder being converted to *sulphate* by fusion with niter and potassium carbonate. This is proof that the protein molecule contains at least 2 atoms of sulphur. Under oxidizing agencies profound changes occur, the products being acids, aldehyds, ketones, amino-acids, hydrocyanic acid, carbon dioxid, and ammonia.

Agents which cause hydrolysis, such as ferments and dilute acids, split up the simple proteins into other proteins of lower molecular weight—proteoses and peptones—which no longer coagulate when heated, and which, owing to the diminished size of the molecule, readily diffuse. The final products of hydrolytic cleavage by ferments or prolonged boiling with acids are of known constitution, are supposed to be preformed like the stones in a building, and in time a study of them as nuclei may lead to a knowledge of their mode of union in the protein molecule. They are the *monoamino-acids*, such as leucin, glycocoll, and alanin; the *amino-diacids*, aspartic and glutamic; the *diamino-acetic* and *diamino-valerianic acids* (ornithin); the dipeptids, *prolin* and *oxyprolin;* the oxyacid, *serin;* the *hexon bases* or *diamino-acids*, lysin, arginin, and histidin; the *isocyclic nuclei* of tyrosin and phenylalanin; the *heterocyclic nucleus* of tryptophan; the *carbohydrate nucleus*, glucosamin; the *sulphur compound*, cystin. Each *a*. acid has the acid group COOH at one end and the basic amino-group NH_2 substituted for a hydrogen atom on the nearest carbon atom. The rest of the compound may be regarded as a radical either of the open chain or the cyclic series. The general formula then may be stated as:

$$R-\overset{\diagup NH_2}{CH}-COOH.$$

Thus, if H be the radical represented by R, then we have the structural formula for glycocoll, $H\,.\,CH\,.\,(NH_2)\,.\,COOH$; if CH_3 be the radical R, then we have alanin, $CH_3\,.\,(NH_2)\,.\,COOH$. Formulas for the others are found on pp. 505, 506.

It is possible for the acid group of one to unite with the basic group of another in an indefinite number of permutations. The various proteins have different kinds, numbers, and arrangements of these relatively few amino-acids.

Putrefaction is the breaking up of proteins by the growth of certain bacteria, the fetid products of intestinal putrefaction

being phenol, indol, skatol, ptomains, volatile fatty acids, methyl mercaptan, ammonia, and hydrogen sulphid. Part of the phenol and skatol are absorbed, and in the liver are joined or conjugated with potassium-acid sulphate, being finally eliminated by the urine. The other end-products remain for a while in the intestines and are ejected as feces and flatus (p. 397).

Coagulation.—The simple soluble proteins, when acidulated and heated, become denatured into insoluble material. The process of change is called *coagulation.* The original substance cannot be reproduced by any manipulation of this white insoluble solid, which in this respect differs from a precipitated protein. The different proteins coagulate at different temperatures; none coagulates by heating alkaline solutions. Complete coagulation requires the combination of heat applied to an acid solution containing 5 per cent. of neutral salts. (See Albuminuria.)

Precipitation in an insoluble combination is produced by adding the mineral acids, especially nitric acid; by some organic acids in strong solutions of neutral salts; by potassium ferrocyanid with acetic acid; by acid solution of tannin; by picric acid, carbolic acid, salicylsulphonic acid, trichloracetic acid, by sodium tungstate; by phosphomolybdic acid, by potassiomercuric iodid; by solutions of metallic salts, such as mercuric chlorid, cupric sulphate, lead acetate, and silver nitrate; by alcohol and chloral; by saturated ammonium sulphate, which precipitates all except peptone.

Experiments.—Having made a solution of albumin by shaking white of egg in a bottle with five times as much water, and separating the sediment, proceed to show coagulation by heat, acids, and by the other reagents named above. Using fresh portions each time, apply the following tests also.

Color Reactions.—Any protein, such as the glutin in dry bread, will give the *xanthoproteic reaction,* which is the yellow color caused by the action of concentrated nitric acid, changing to orange on the addition of excess of ammonium hydroxid. This indicates the presence of the benzene ring, and is given by tryptophan, tyrosin, or phenylalanin (pp. 463 and 506).

Biuret Reaction.—A violet to pink color obtained when a hot Fehling's solution is overlaid with the protein—after complete hydrolysis the products do not give this reaction.

Fröhde's Reaction.—A solution of molybdic acid in sulphuric acid gives to solid proteins a blue color (p. 522).

Millon's Reaction.—This reagent (mercuric nitrate) imparts a purple-red color to pieces of solid proteins when they are heated in it. It is also given by the phenol group in the tyrosin nucleus (pp. 461 and 506).

Liebermann's reaction is the violet-blue color obtained when proteins are dissolved in boiling hydrochloric acid.

Adamkiewicz's reaction requires the solution of the protein in hot glacial acetic acid. When cool, it is overlaid with concentrated sulphuric acid. A violet or purple band appears at the line of contact. It is due to the tryptophan group (p. 506).

Molisch's reaction (p. 474) indicates glucosamin or some other carbohydrate (p. 435).

Ninhydrin reaction (p. 467) indicates proteins, peptones, polypeptids, and α-amino-acids (except prolin, oxyprolin, and pyrrolidin-carbonic acid.

FALLACIES.—The positive detection of a protein requires all of these color reactions. No one of them can be considered as characteristic, as similar colors are caused by alkaloids and other nitrogenous organic substances.

Classification of Proteins.—There are three groups of animal proteins: Simple Proteins, Conjugate Proteins, and Derived Proteins: I. SIMPLE PROTEINS—(1) *Protamins;* (2) *Histons;* (3) *Albumins;* (4) *Globulins;* (5) *Scleroproteins;* (6) *Phosphoproteins.* II. CONJUGATE PROTEINS—*a*, chromoproteins; *b*, glucoproteins; *c*, nucleoproteins. III. DERIVED PROTEINS—*a*, infraproteins; *b*, proteoses; *c*, peptones; *d*, polypeptids.

1. PROTAMINS.—In the heads of the spermatozoa of fish are found nucleoproteins which yield basic substances that resemble simple albumins in some reactions, though not in all. Their molecules contain the groups that give the biuret reaction and are precipitated like alkaloids, but not the groups that coagulate when heated and respond to Millon's reagent. They yield only a small number of amino-acids on hydrolysis. Hence they are regarded as the simplest of all proteins. They are called *protamins* and differ according to their source; thus, *salmin* (salmon), $C_{30}H_{57}N_{17}O_6$; *sturin* (sturgeon), $C_{34}H_{71}N_{17}O_9$, etc. When hydrolyzed by trypsin they first yield substances analogous to peptone called *protons*, and finally split up into simpler products, among which are bases containing 6 atoms of carbon, *hexons*, named histidin, $C_6H_9N_3O_2$; arginin, $C_6H_{14}N_4O_3$; and lysin, $C_6H_{14}N_2O_2$. As the more complex proteins also yield hexons, it is probable that all contain a protamin nucleus.

2. HISTONS.—These closely resemble the protamins, differing in the complexity of the molecule, which in histons is more like that of a pure albumin in a simpler form. The protamins seem to be constituents of the more highly developed histons, which yield a greater number of amino-acids on hydrolysis. Histons are like the albumoses in their reactions, are basic, and most of them contain iron. Among them is *globin* of the red blood-corpuscle and

nucleohiston from the thymus gland of the calf (p. 539). They are distinguished by being precipitable with ammonia.

3. Albumins.—These dissolve in pure water, coagulate when heated, and precipitate from solutions saturated with ammonium sulphate. They include serum-albumin of the blood, ovalbumin of egg, lactalbumin of milk, and myo-albumin of muscle.

4. Globulins.—These do not dissolve in pure water, but are soluble in a 0.5 to 1 per cent. solution of neutral salts, coagulate by heat, precipitate from solutions saturated with magnesium sulphate or sodium chlorid, or by addition of an equal volume of saturated solution of ammonium sulphate. They include serum-globulin, lactoglobulin, myoglobulin and its derivative myosin, fibrinogen and its derivative fibrin of clotted blood.

5. Scleroproteins.—Under this head are grouped the proteins, which differ somewhat among themselves and yet are alike in resisting the action of the agents which dissolve the other proteins referred to above. They are the horny, elastic, tough, gelatinous substances found in bone, cartilage, connective tissue, epidermis, hair, etc. The list given below contains the important members of skeletal origin.

Keratins are characteristic of the skin, hair, and nails. They are rich in loosely combined sulphur, which appears to take the place of oxygen in a simple protein, and which forms a black sulphid with lead hair-dyes. They are not affected by gastric juice or trypsin, but dissolve in warm caustic alkalis. They dissolve in water heated under pressure to 150°–200° C. (302°–392° F.), but do not gelatinize. They respond to the xanthoproteic and Millon's reactions.

Elastins are found in the yellow elastic tissue of ligaments. They are digested by the gastric juice and by trypsin; are insoluble in water unless heated under pressure; are soluble in nitric acid and in boiling alkalis.

Collagens may be considered under two varieties: *ossein* of bone and *chondrogen* of cartilage and tendons. Dry collagen is yellow, hard, and insoluble. By boiling in water or dilute acid it swells up and forms gelatin or glue, which makes a clear solution, turning to jelly when cooled. *Gelatin* is soluble in gastric juice and trypsin, but is not coagulated by heat nor precipitated by acetic acid. It is precipitated by hydrochloric acid, phosphotungstic acid, and bromin water. Collagen unites with tannic acid in the form of a tough and durable substance, common leather. Gelatin responds to the biuret and xanthoproteic reactions, but not to Millon's.

6. Phosphoproteins.—Vitellin of egg and caseinogen with its derivative casein are members of this group. *Caseinogen*, the principal protein of milk, by the action of rennin, yields the casein

of cheese. Boiling does not coagulate it, but causes it to split off some sulphur and lessens its digestibility. It contains phosphorus, but no carbohydrate group, the latter being supplied to the suckling by the lactose of the milk. Casein contains phosphorus in direct combination with the protein and not in a nucleic acid group, as in the nucleoproteins.

II. CONJUGATE PROTEINS.—This class includes the proteins which are capable of being decomposed into a simple protein and some other substance of different character. The non-protein substances yielded by the splitting give the character and name to the subclasses in which they are grouped; thus, they are hemoglobins, glucoproteins, phosphoglucoproteins, nucleoproteins.

a. **Chromoproteins.**—The typic compound is the hemoglobin, which gives color to the blood and carries oxygen to the tissues. In the corpuscles it exists as an insoluble amorphous combination, constituting 40 per cent. of their weight. When free it is readily soluble in water, insoluble in alcohol and ether, and crystallizable in beautiful red crystals which differ in shape in the hemoglobin of different animals. The form of combination found in asphyxia is called *common* or *reduced* hemoglobin; that in ordinary arterial blood, richer in oxygen, is called *oxyhemoglobin.* Owing to its remarkable capacity for absorbing gases in a loose combination it is an easy matter to convert one into the other by means of oxidizing and reducing agents.[1] The proportion of the two hemoglobins in venous blood is intermediate between that in arterial blood and that in the dark blood of asphyxia. The absorption power for carbon dioxid, carbon monoxid, hydrogen sulphid, and hydrocyanic acid results in combinations which not only poison the tissues, but also interfere with the normal absorption powers for oxygen. When a solution of hemoglobin is heated to 70° C. (158° F.) or hydrolyzed by acids or alkalis, it splits into the simple protein, *globin,* and a colored derivative containing iron, *hematin* (pp. 534, 537).

The empiric formula for the hemoglobin of the dog is—

$$C_{758}H_{1203}N_{195}O_{218}FeS_3.$$

Hematin, unlike the globin, dissolves in acidified alcohol and dries in a blue-black powder which, with hydrochloric acid, forms *hemin* crystals (Plate 4, Fig. 3), a characteristic test. (See Hematuria.)

$$\underset{\text{Hematin.}}{C_{34}H_{34}N_4FeO_5} + HCl \rightarrow \underset{\text{Hematin or chlorhematin.}}{C_{34}H_{33}N_4O_4FeCl} + H_2O$$

[1] The dissociation that occurs in the blood under normal conditions is represented as a reversible process in this equation:

$$\text{Oxyhemoglobin} \rightleftharpoons \text{Hemoglobin} + \text{Oxygen}$$

It is met with in the blood and in the urine after poisoning from hydrogen arsenid. In alkaline solutions its spectrum gives a single, poorly defined absorption band extending from C to D (Plate 4, f and h).

Spectroscopic Tests.—The best method of distinguishing the several hemoglobins is by their absorption spectra, shown in Plate 4.

Oxyhemoglobin gives a spectrum which varies with the degree of dilution of the arterial blood used for the observation. The blood is opaque when observed in a vessel of usual thickness, but when diluted, permits more and more light to pass until the red, orange, and green colors appear with a band in the green (Plate 4, b). Further dilution permits the typic double band to appear to the right of the D line (Plate 4, a). This characteristic spectrum is discernible even when the observation is made on a layer, 1 cm. thick, of a solution 0.01 per cent. in strength.

A change takes place, to reduced or common hemoglobin, by the action of *Stokes' reagent* (ammoniacal solution of ferrous tartrate)[1] or other reducing agent (Plate 4, c).

Reduced hemoglobin shows a spectrum with a single broad band to the right of the D line (Plate 4, c). Agitated with air, the solution absorbs oxygen until all the reduced hemoglobin is converted to oxyhemoglobin, changing in color from purple to red.

Methemoglobin is a brownish, soluble substance produced when oxygen is united with hemoglobin in a form less readily separable than in oxyhemoglobin. It occurs in blood that has decomposed or that has been treated with various reagents like amyl nitrite or potassium ferrocyanid. In the body it is found in bloody transudates and cystic contents; also in the blood of the vessels and in the urine in hematuria following poisonous doses of antipyrin, phenacetin, potassium chlorate, and amyl nitrite. In neutral fluids its spectrum shows a band between C and D like that in Plate 4, g, connected by shading with one of the bands of Plate 4, d. When in a weak solution faintly alkaline with ammonia, as in stale urine, the spectrum is different, the line between C and D moving to the right (Plate 4, d). Reducing agents change the spectrum of its alkaline solutions to that of reduced hemoglobin (Plate 4, c).

Hematoporphyrin.—When hematin is treated with sulphuric acid that has been saturated with hydrobromic acid, the iron is split off, and the remainder, iron-free, is a new dark pigment, hematoporphyrin:

$$\underset{\text{Hematin.}}{C_{34}H_{34}N_4FeO_3} + 2HBr + H_2O \rightarrow \underset{\text{Hematoporphyrin.}}{C_{34}H_{38}N_4O_6} + FeBr_2 + H_2.$$

[1] *Stokes' reagent:* Mix ferrous sulphate, 3 gm., with 3 gm. of tartaric acid dissolved in water, and add water to 100 c.c. Before using, add enough ammonia water to dissolve the precipitate and leave an alkaline reaction.

PLATE 4.

BLOOD-SPECTRA AND BLOOD-CRYSTALS.

FIG. 1, a. **Normal Solar Spectra**, with the various absorption-lines marked by letters (A, B, C, D, a, b, *a*). The blood changes the spectrum of the light passing through (marked dilution of the blood is necessary) in such a way that, in accordance with the behavior of the hemoglobin present, various portions of the colored spectrum are obliterated or absorbed. There thus appear at various places black bands of varying thickness.

b. Spectrum of blood rich in oxygen (oxyhemoglobin-spectrum) (two bands between D and E).

c. Spectrum of reduced hemoglobin.

d. Spectrum of methemoglobin weak solution, faintly alkaline with ammonia (accompanying hemoglobinemia, destruction of the red blood-corpuscles through poisoning with potassic chlorate, pyrogallol, sulfonal, toadstools). Without the alkali, methemoglobin gives in addition an absorption band between C and D, as shown in Fig. g.

e. Spectrum of reduced CO-hemoglobin. The reduction accompanying carbon-monoxid poisoning is unattended with disappearance of the two bands between D and E; in contrast with reduced oxyhemoglobin (Fig. c).

f.–h. Spectra of hematin in acid and alkaline solutions and reduced (occurs in urine).

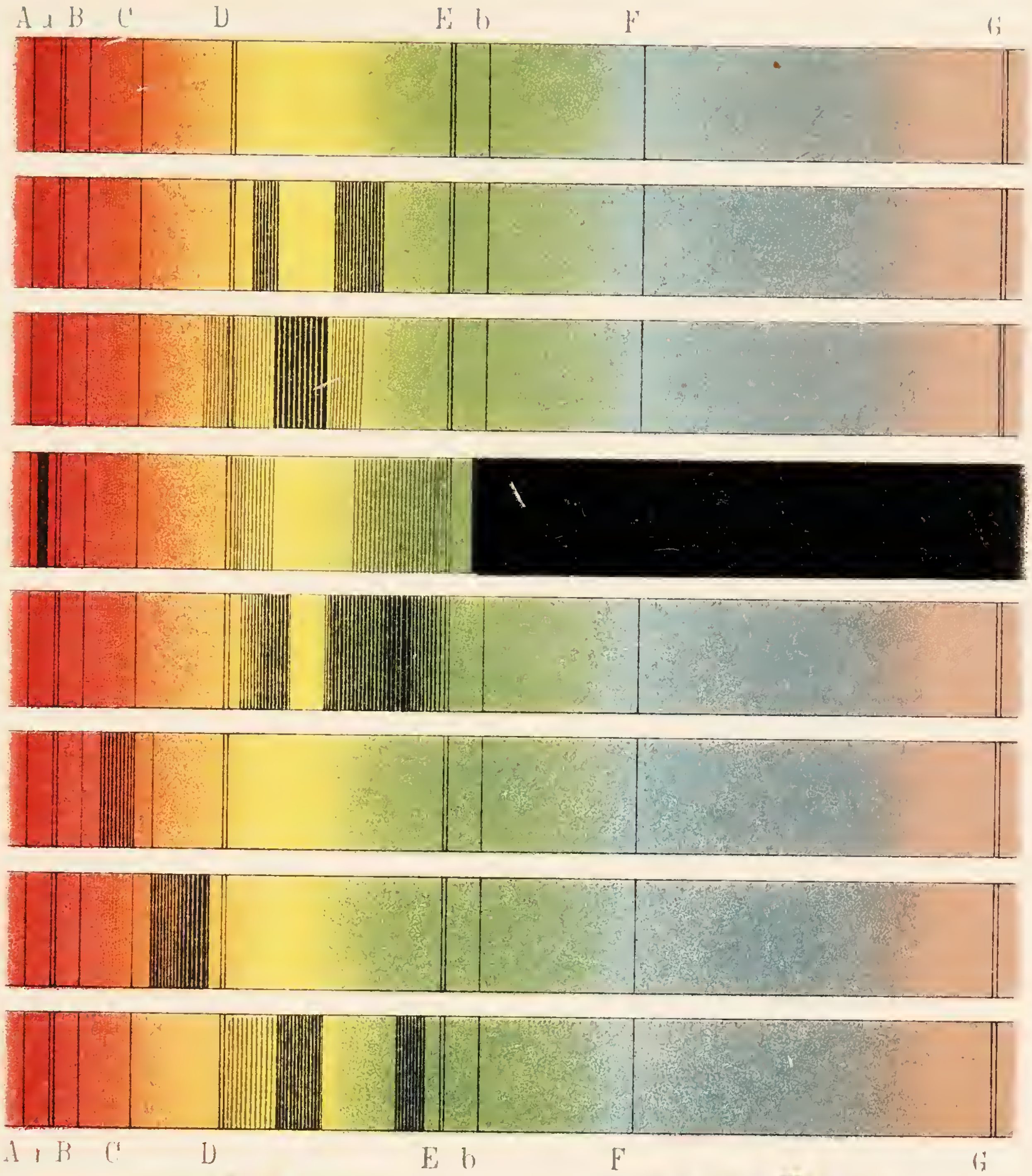
FIG. 2. **Hematoidin Crystals** (from old hemorrhagic focus).—Partly in rhombic plates, partly in granules.

FIG. 3. **Teichmann's Hemin-crystals.**—They serve for the demonstration of even slight traces of blood, old or recent. They are obtained by adding to the remnant of blood a crystal of sodic chlorid and a drop of glacial acetic acid, and effecting evaporation by gentle heat. Their recognition is of importance from a medico-legal point of view.

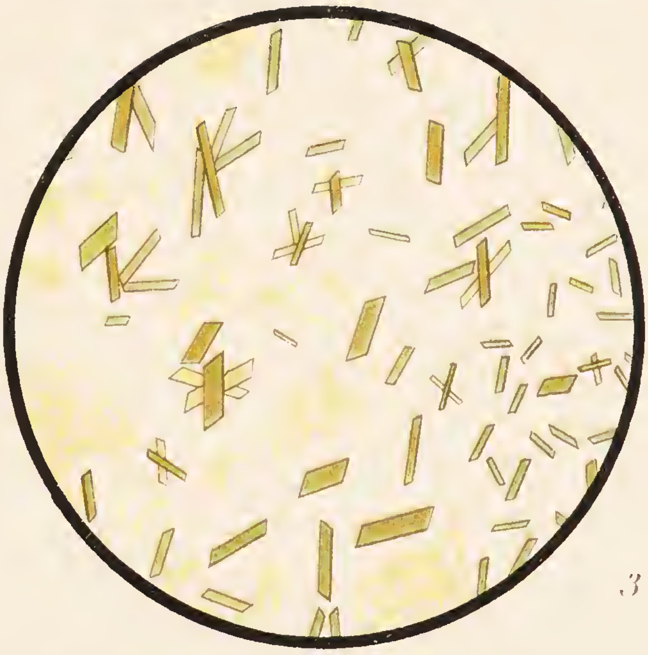
(JAKOB.)

PLATE 4.

1



2



3

like starch, turn blue on being treated with sulphuric acid and iodin. They color red-brown with iodin alone; bright red with eosin; and red with anilin green. Amyloid is insoluble in water, amorphous, white, not dissolved in gastric juice, and responds to the xanthoproteic, biuret, and Millon's reaction.

Phosphoglucoproteins are compound proteins rich in phosphorus, which differ from nucleo-albumin and nucleoprotein in been hydrolyzed into reducing substances with no xanthin bases (see p. 496).

c. **Nucleoproteins** are rich in phosphorus, and by hydrolysis break up into a protein and a true nuclein. Nuclein splits again into a protein and nucleic acid, and the nucleic acid decomposes into pyrimidin bases, phosphoric acid, purin bases, and a carbohydrate. *Nucleohiston* is a variety present in the thymus gland. Nucleoproteins are necessary to cell life in general, especially to the nucleus, and are present in all the glandular organs, the spermatozoa, pus-cells, and yeast plant. They are not dissolved by gastric juice. In reaction they are weak acids, forming soluble salts with bases. They are coagulated by heat. They probably constitute the chief mass of the protein in cell substance and are most important in relation to cell activity.

Nucleoproteins are distinguished by the products obtained after hydrolysis, namely:

True cell nucleins, which pass from dead cells into the animal fluids. They yield proteins and nucleic acid, which latter in turn splits into phosphoric acid and purin bases. Gastric digestion of nucleoproteins leaves them as insoluble residues. As purin bases contribute to the formation of uric acid (p. 496), a regimen of food for patients having the uric-acid diathesis reduces the meat allowance to a minimum.

Nucleic acids are set free by the decomposition of nucleins with alkalis. They break up into phosphoric acid, pyrimidins, and purins. They differ in the bases they contain. All are white, amorphous, insoluble in pure water, acid in reactions, forming soluble salts with alkalis. They are precipitated by acetic acid and are found in the insoluble residue left when a nucleoprotein is treated with gastric juice.

III. Derivatives of Proteins.—Of these, the products of protein-hydrolysis by enzyms and chemicals are those requiring special attention.

a. **Infraproteins** or **metaproteins** are derived from native proteins by digestion with alkalis or acids. They do not dissolve in salt solution nor in cold water except when a small amount of acid or of alkali is present. Heat does not coagulate the solution, but the albuminate is precipitated by neutralizing it. Saturation of the solution with

sodium chlorid or ammonium sulphate causes precipitation from the acid solution, but does not affect the solution in alkali. When the alkalis act on native proteins they separate nitrogen and sulphur from the molecule; hence an alkali albuminate is not convertible into an acid albuminate, which should contain those elements. Alkalis may act on acid albuminates to change them to alkali albuminates. An alkali albuminate in water containing calcium carbonate dissolves with escape of carbon dioxid. It has acid properties which are not shared by acid albuminates.

During gastric digestion the hydrochloric acid changes myosin of muscle tissue to *syntonin*, a form of acid albuminate.

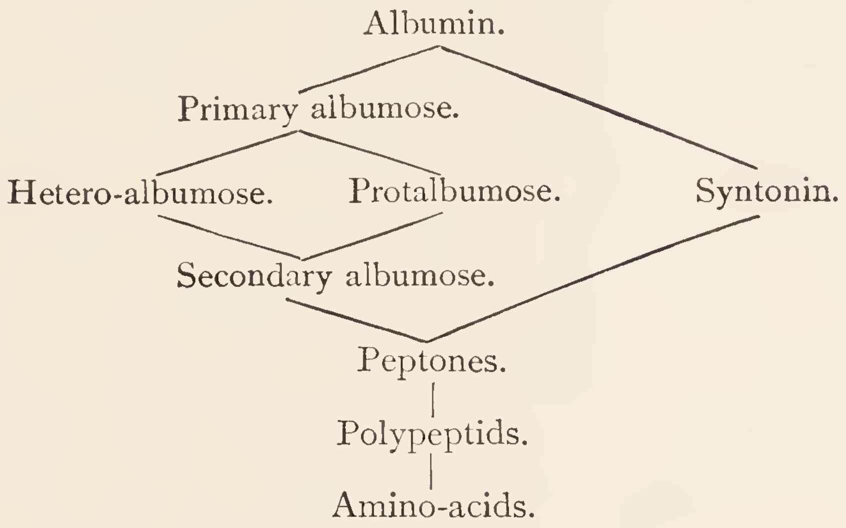
Coagulated proteins are produced from native protein by heat, acids, alcohol, and other reagents, and by enzyms. Neither the process nor the product is understood. Hard-boiled white of egg and fibrin are examples. They are insoluble in pure water, in dilute acids, alkalis, and solutions of neutral salts. By the enzyms of digestion they are changed to peptones and albumoses. *Fibrin* is the white solid protein which appears in clotted blood. A ferment coagulates the dissolved fibrinogen of the plasma. Similar coagulated proteins have been found in the liver and other glands.

b. **Proteoses or Albumoses.**—In the digestion of proteins the final protein-like substance is called *peptone*. The process of change is one of successive acts of hydrolysis—splitting up the molecule. It has many intermediate stages, which are recognized by the characteristic proteins derived by the action of the acids and enzyms of animal digestion. *Syntonin* or *acid albuminate* has already been referred to; the others are grouped under the general head of *proteoses*, *propeptones*, or *albumoses*. All the proteoses are soluble in pure water, non-coagulable by heat, precipitated from solution by saturation with ammonium sulphate.

The proteoses are considered under two classes: *primary* and *secondary*. The *primary* includes *protoproteoses* and *heteroproteoses;* the former in its reactions with neutral salts resemble the native albumins, while the latter are like the globulins. The primary proteoses are precipitated by 50 per cent. ammonium sulphate in acid solution; the secondary require for precipitation a saturated solution of ammonium sulphate. Heteroproteose is precipitated by saturated neutral sodium chlorid, while protoproteose requires saturated acid sodium chlorid.

The *secondary proteoses* are derivatives of the primary varieties by hydrolytic splitting, and are not precipitated by cupric sulphate. Having fewer albumin reactions, they represent further cleavage. They are closely related to the peptones. The proteoses differ somewhat according to the native protein from which they are derived, the parent substances giving the name—as, *albumose*, *globulose*, *vitellose*, *caseose*, etc.

c. **Peptones.**—The last of the products of hydrolysis of albumins that retain albuminous characteristics are the peptones. They closely resemble each other, the difference being unimportant. The stages of hydrolysis giving the cleavage products of albumin are shown in this scheme, where all the proteoses (albumoses) are seen to end in peptones which are practically of one kind:



Peptones are very soluble in water, dialyzable, not coagulated by heat, not precipitated by ammonium sulphate or by nitric acid, with or without neutral salts. In common with other proteins they are precipitated by strong alcohol, phosphomolybdic acid, mercuric chlorid, and tannin, and give the biuret reaction.

d. **Polypeptids.**—Beyond the stage of peptone in the cleavage series given above are certain products which consist of two or more amino-acids linked together. Some of them give the biuret reaction. The majority of the polypeptids are synthetic products containing from 2 to 7 different amino-acids. They are optically active, like the natural proteins, give the biuret reaction, are precipitated by phosphotungstic acid, and are split by trypsin into the same hydrolytic products as those yielded by protein. An artificial peptid, glyzylalanin, has been made identical with that obtained from natural silk fibrin.

The stages of hydrolysis, by which protein is disintegrated through the action of proteases, are paralleled by those through which starch is progressively simplified when hydrolyzed by digestive enzyms. Thus:

Starch → Soluble starch → Dextrins → Maltose → Glucose.
Proteins → Proteoses → Peptones → Polypeptids → Amino-acids.

Changes of Proteins in the Body.—As saliva contains no enzym capable of causing chemical change in the proteins, they pass to the stomach unaltered, except by the disintegrating and dissolving effects of mastication. Both the soluble and coagulated proteins need to be digested in order to produce absorbable substances.

These dialyzable products are the result of a series of hydrolytic reactions by which the complex protein is broken up into simpler compounds. In the stomach by the action of pepsin and acid they change into acid albumin, proteoses and peptones, successively increasing in solubility and diffusibility with each form. In the small intestine the enzym *trypsin* splits the protein by hydrolysis, as does the pepsin, only more rapidly, and the medium is alkaline. The remainder in the large intestine undergoes hydrolysis by *erepsin* and putrefaction by bacteria. The products of these cleavages of the protein molecule are, successively: proteoses, peptones, amino-acids, glucosamin, hexon bases, cystin, indol, skatol, phenol, and paracresol. The amino-acids and hexon bases, after absorption, are synthesized to make the protein tissue materials. The four last-named products, for the most part, pass out with the feces, but to some extent are absorbed into the portal blood. Their poisonous properties are destroyed in the liver, where they meet potassium sulphate, which unites with them to form the conjugated sulphates excreted later by the kidney. As potassium sulphophenolate and potassium indoxyl sulphate, etc., they are harmless.

It is probable that the absorbed products split off a carbohydrate from the glucosamin, which is easily converted to glycogen, dextrose, or even fat.

The carbohydrate and fat are held closely to the protoplasm of the cells and are used by it as sources of energy.

The larger proportion of the body proteins is contained in the muscles. In them metabolism is continuous, the massive protein molecule not breaking down to free nitrogen, carbon dioxid, and water, but chiefly into *ammonium* salts, lactate and carbamate, and partly into glycocoll and other amino-acids with creatin, which ultimately changes to creatinin and ammonium lactate. All of these, on passing through the liver, change to urea, which ultimately escapes in the urine (p. 498).

The sulphur of the proteins is oxidized finally to mineral sulphates, part of which are eliminated by the kidneys as such and part joins in the liver to the aromatic radicals, phenol, indol, and skatol, as stated above.

Nucleoproteins in other tissues are much less abundant than the muscle proteins. They are found chiefly in the gland cells and split into true protein and nucleic acid, which later breaks down into phosphoric acid and the purin bases. The latter ultimately in the liver oxidize to the uric acid of the urine. Thus, the metabolism of gland cells produces uric acid as regularly as muscle substance forms urea.

The small amount of hippuric acid found in urine is derived partly from food and partly from the oxidation of aromatic groups

of protein metabolism into benzoic acid. In the kidney the benzoic acid is joined with glycocoll to form hippuric acid, and is then excreted.

FERMENTS OR ENZYMS

Fermentation is the transformation of an organic substance produced by an enzym acting by catalysis (p. 396). The enzym is secreted in the living body by cell action or is produced by the processes of nutrition of low organisms. At one time these organisms—bacteria, molds, etc.—were called the *true* ferments, and their soluble enzyms called *false* ferments; but it is now established that the living molds act because they contain the ferment, and the true agent in every case is the soluble enzym. Moreover, this product of cell life can manifest its special activity after the death of the parent cell. We cannot be sure that any enzym has as yet been isolated in a chemically pure form. They are commonly regarded as albuminous, but this may be only an appearance due to the adherent particles of protein matter. They are soluble in water, dilute glycerin, dilute alcohol, and solution of sodium chlorid, yet are not diffusible, and are precipitated by ammonium sulphate or strong alcohol. It is probable that some of them are colloidal combinations of organic substances with metal ions, such as manganese and iron. They are identified by their end products.

Enzyms are very *susceptible* to certain external influences. Although they resist dilute solutions of poisons, such as chloroform, thymol, salicylic acid, arsenous acid, boric acid, and glycerin, they are paralyzed by $HgCl_2$,HCN, carbolic acid, and sulphites. Their action is arrested by absence of water, to be restored when moisture is abundant. As a general rule, the animal ferments, when moist, are killed by a temperature of 75° C. (167° F.), and the vegetable ferments by 80° C. (176° F.). When dry they may withstand a temperature of 150° C. (302° F.). All are destroyed by boiling in water and by any but weak concentrations of acids and alkalis. They are most active at the temperature of the animal body between 35°–45° C. An enzym selects specifically the substance upon which it works. Thus, one decomposes a certain sugar of an isomeric group, but does not affect the others, almost identical. This enzym must have a stereochemical structure related to the stereochemical structure of the sugar, as a key fits into a lock.

The **functions** of the enzyms are specific and well understood. In most cases they *hydrolyze*, *i. e.*, cause a reaction with water, ending in cleavage of the substance upon which they act. In other cases they are concerned with the *oxidations* of the tissues. In some way they communicate such disturbances to the complex albuminous or polysaccharid molecules as to lead to simpler and more

stable combinations. In this they act like the *catalyzing* colloidal solutions of metals, which accelerate certain reactions (p. 87). In all cases the amount of transformation is out of proportion to the quantity of the agent, and the agent is not used up, as it takes no part in the reaction. Colloidal platinum breaks up 1,000,000 times its quantity of hydrogen peroxid and remains as strong as ever. It also inverts cane-sugar, like *sucrase* or *invertase*, and acts on certain fats like a fat-splitting enzym. The poisons which inhibit the enzyms, such as mercuric chlorid and hydrocyanic acid, also paralyze the catalytic action of colloidal platinum.

Among the agents allied to these *anticatalyzers* are the *antienzyms*, such as *antirennin*. This "anti" body is developed in the serum and milk after repeated intravenous injections of rennin solution. It inhibits the clotting action of the enzym upon the caseinogen of milk. During life the gastric mucous membrane is protected from self-digestion by its *antipepsin*. It is suspected that the other enzyms are antagonized by similar "anti" substances just as the toxins have their antitoxins.

Enzym action is not only one of decomposition, but also may at times be one of construction. Maltose is not completely changed by its enzym into glucose, but only up to a point of equilibrium. Using concentrated solutions of pure glucose, the same ferment reverses its action and builds up maltose to the same point of natural equilibrium between the fermented substance and its products. The fat-splitting lipase causes not only the hydrolysis of ethyl butyrate into alcohol and butyric acid, but, with a change in the acting masses, also the reverse synthesis of alcohol and acid into the ester. Thus the same enzym may split or may build up fats according to the concentrations present. Fat is digested by steapsin in the intestine only when the resulting glycerin and fatty acids are removed as they are formed. In the fluids of the tissues, on the other hand, the glycerin and acids are in excess, the activity of the enzym is reversed, and fat is deposited. During starvation the lipase acts directly on the fat deposits and the fatty acids and glycerin of the cells diffuse into the blood. From this it appears that the intracellular enzyms not only break down and clear away effete matter, but act synthetically and probably maintain the normal equilibrium between the cell contents and the serum of blood or lymph (p. 83).

It is now established that enzyms are omnipresent in the cells (*intracellular enzyms*) and take part in almost all chemical changes in the living body. The liver-cells alone exhibit such varied catalytic powers that we must assume the presence in them of twenty different enzyms. Only the principal groups concerned in digestion, nutrition, and secretion are referred to in the list on p. 545.

Nomenclature.—In order to simplify the nomenclature, it is proposed to attach the suffix *-ase* to the stem of the name of the substance upon which it acts; thus, *sucrase* is the specific enzym of *sucrose*. The adjective is made by *-lytic* suffixed to the stem, thus: *peptolytic* enzyms are those that decompose peptones, and the process of cleavage is called a *-lysis*; thus *peptolysis* means the splitting up of peptone.

Classification.—A good basis for grouping the ferments is found in their specific functions and the products of their action. Four classes of great interest are those which hydrolyze the food-stuffs, proteins, carbohydrates, and fats. In the following arrangement they are mentioned first:

Proteases (*Proteolytic Enzyms*).—Pepsin of the stomach and trypsin of the pancreas are digestive ferments which break up the complex non-dialyzable protein molecules into proteoses and peptones. Erepsin, which is found in the intestinal mucus, hydrolyzes proteoses to amino-acids. The power of self-digestion, shown by the antiseptic tissues after death, is due to autolytic proteases (pp. 523 and 545).

Amylases (*Amylolytic Enzyms*).—Ptyalin of the saliva, the diastases of the pancreas, of the liver, and of vegetables, hydrolyze the starch molecule and split it into a disaccharid maltose, with dextrin as an intermediate product (pp. 551 and 564).

Invertases (*Inverting Enzyms*).—In the saliva, in the pancreatic, and in enteric juices ferments are found which invert the disaccharids to monosaccharids, saccharase acting on cane-sugar, maltase on maltose, lactase on lactose (p. 565).

Lipases (*Lipolytic Enzyms*).—The hydrolysis of fats to fatty acids and glycerin is accomplished by the steapsin of the pancreas and also by lipases in the gastric juice and the tissues generally as intracellular enzyms (pp. 553 and 565).

Urases are enzyms that hydrolyze urea into ammonium carbonate. They are secreted by various bacteria that excite ammoniacal fermentation in stale urine (p. 599).

Nucleases are enzyms in the tissues which split nucleic acid into phosphoric acid and the purin bases (p. 498).

Next in point of interest come the enzyms, the special action of which is to oxidize albuminous substances in the cells.

Oxidases (*Oxidizing Enzyms*).—The oxygen carriers are divided into three groups, two of which, oxygenases and peroxidases, yield oxygen to other substances and then immediately reoxidize themselves. The third, catalases, cannot reoxidize themselves from the air.

Oxygenases turn tincture guaiac blue by direct transference of the molecular oxygen of the air.

Peroxidases are bodies which contain manganese, aluminium, iron, and possibly copper. They are quite stable and do not oxidize directly, but only in the presence of peroxids. Only on the addition of hydrogen peroxid will they turn guaiac blue.

Catalases are the agents in protoplasm which decompose hydrogen peroxid so that the peroxidases can utilize the liberated oxygen. They do not turn guaiac blue directly nor in the presence of hydrogen peroxid.

Guaiac Test for Oxidases.—Make a fresh tincture of guaiac by boiling pieces of guaiac with alcohol in a test-tube. When a deep yellow color is developed, filter and add a few drops of the filtrate to water until a milky emulsion is formed. A slice of raw potato indicates the presence of *oxygenases* by turning the emulsion blue. If, instead of potato, some blood or raw meat, minced, containing *peroxidases* be immersed in the emulsion, there is no change until hydrogen peroxid is added, when the blue reaction appears. If bubbles of free oxygen form on the tissue after the peroxid is added, *catalases* are present.

Coagulases (*Clotting Enzyms*).—These comprise *thrombase*, which coagulates the fibrin of the blood; and *rennin*, which curdles milk. As calcium salts are necessary for their action, it is probable that the clot is a calcium compound of fibrin or casein (pp. 554 and 571).

Having a very different chemical effect are:

Reductases (*reducing enzyms*), such as the one that reduces sulphur to hydrogen sulphid.

Glucosid-splitting enzyms play an important part in certain medicinal plants. Mention has been made (pp. 446 and 468) of the action of emulsin or *synaptase* upon amygdalin. Another example is the action of *myrosin* upon the sinigrin (myronic acid) of mustard seed, which develops allyl mustard oil.

On the other hand, *synthesis* of amygdalin can be brought about by the enzym maltase acting upon mandelic nitrile and glucose:

$$\underset{\text{Mandelic nitrile.}}{C_{14}H_{17}NO_6} + C_6H_{12}O_6 = \underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + H_2O.$$

Bacteriolytic enzyms split up their media by secretion of bacilli, such as those of lactic and butyric acids (pp. 421, 448).

Autolytic enzyms are found in the tissues generally. They are supposed to split proteins into nitrogenous bases, such as the purins (pp. 496–499). *Guanase*, of the thymus gland, adrenals, and pancreas, converts guanin to xanthin. *Adenase*, of the spleen, liver, and pancreas, converts adenin to hypoxanthin. The breaking-up process continues in the liver and spleen until uric acid is produced,

and this itself is destroyed by enzyms. These uricolytic enzyms have been found in the liver, kidney, muscles, and bone-marrow. The uric acid is split by them to glycocoll, allantoin, and oxalic acid.

Normal *milk* has enzyms favorable to the digestion of the milk (p. 580). *Alcoholic* and *acetous* enzyms are described on pp. 421, 452.

PROTECTIVE ENZYMS

When a foreign protein is injected into the blood it provokes a protective response. The plasma acquires the power to split that particular protein molecule into simpler ones that are harmless. The biologic change has called into play enzyms ordinarily missing from the blood, which have a specific digestive property tending to destroy or to utilize the abnormal intruder. Albumins give rise to proteolytic enzyms, cane sugar to an inverting enzym. Substances which are native to some part of the system but foreign to the blood, owing to physiologic or pathologic changes, may be absorbed into the blood and excite similar responsive enzyms. Free chorionic villi of an impregnated ovum induce a reaction which produces digesting enzyms in the blood for placental tissue, which may be detected by tests for the cleavage products. The technic of *Abderhalden's test* is very elaborate, calling for assiduous care of every detail. Briefly stated, it is as follows:

Sero-diagnosis Test for Pregnancy.—Of fresh clear blood-serum from the patient taken fasting, 2 or 3 c.c. are mixed with 1 gm. of specially preserved placental tissue in a diffusion tube of parchment (Schleicher and Schull, No. 579) and dialyzed against 20 c.c. of distilled water in a small glass cylinder. Both liquids are covered with toluol, and the operation of digestion is conducted for twelve to sixteen hours in the incubator at 37° C. (98.6° F.). In that time, if the specific protective enzym exists in the serum it will have attacked the placental protein, but no other, and the cleavage products will have diffused through the dialyzer which is not permeable to the normal albumins of the serum.

Of this clear dialyzed fluid, 10 c.c. are mixed with 2 c.c. of a 1 per cent. aqueous solution of ninhydrin (p. 467) in a test-tube and boiled for one minute. A blue color means that the placental tissue has been digested by its proteolytic enzym contained in the serum, and that the patient must therefore be pregnant. In this way tubal pregnancy may be differentiated from ovarian tumor. The same procedure would demonstrate the presence of other definite proteolytic enzyms developed to combat protein from internal neoplasms. Cancer tissue is used in place of placental when the test is for cancer, and albumin from tubercle bacilli when testing for tuberculosis.

ENERGY OF FOODS

In the preceding pages we have studied the properties of foods and of the proximate principles of the human body, and stated briefly the chemical changes they undergo while subject to the processes of life. These changes in the principles of the organism are incessant. It is necessary to life that the elementary atoms should not remain in stable groups, but forever be moving from one unstable organic form to another. In another place (p. 109) it has been stated that matter is indestructible, and that the forces which move matter are phases of one energy, the total of which is not diminished or increased. The union of carbon and oxygen converts the *chemical* energy of the two separate elements into the measurable *free* energy of heat. Energy under appropriate conditions takes the different forms of light, electricity, magnetism, mechanical motion, or, in the animal body, the collection of forces that constitutes *life*.

From the energies of the sunbeam the leaf of the plant derives power to decompose carbon dioxid. From the earth, by its rootlets, the plant obtains water, nitrates, and other mineral salts. The sunbeams supply energy for the synthesis of these simple substances into the complex molecules of starch, sugar, glutin, oils, etc. These food principles are stores of potential energy for the animal, which reverses the chemical processes, liberating the energy in active forms as the proteins and carbohydrates break up into urea, carbon dioxid, and water. These animal excreta in turn become food for plants (p. 104). The organic food materials which animals take from plants are not assimilable in their original state. After they are eaten they must be altered chemically before they are suitable for absorption. *Digestion* is the sum of the chemical processes preliminary to absorption. *Metabolism* includes the processes of nutrition and secretion taking place after absorption in the fluids and cells of the tissues. They are partly constructive (anabolic) of digested products into protoplasm, and partly destructive (katabolic) of protoplasm into excrementitious substances. Metabolism may be regarded as the efforts of the enzyms to maintain an equilibrium in cell substance which must be continuously readjusted because of the loss of balance due to oxidation or other changes in the components of cells.

Foods.—The substances actually needed by the body to maintain physical and mental strength, health, weight, endurance, and resistance to disease are called foods.

These must be supplied not simply in the minimum amount and proportion to keep an equilibrium between waste and repair,

but with an additional allowance to provide against the danger of under-nutrition when unusual stress occurs. An undue supply above the correct requirements may prove not only wasteful, but even injurious, by the unnecessary tax put upon the katabolic processes and the eliminating organs. The various kinds of food-stuffs used by man have constituents that can be arranged in four groups, viz.: (1) Proteins or albuminous substances; (2) carbohydrates (sugar, starch, etc.); (3) fats; (4) inorganic salts.

Proteins or Nitrogenous Foods.—From both vegetable and animal sources we obtain albuminous substances essential to life, containing, when dry, nitrogen, about 16 per cent. They are abundant in bread, cereals, peas, beans, fish, eggs, and meat. The two last-named, eggs and lean meat, are almost entirely protein. Bread and cereals are composed mostly of the carbohydrate starch, but all have some protein. Flour has 13.5 per cent. protein and fresh green peas 7 per cent. The destiny of protein is to be oxidized for the most part to urea, carbon dioxid, and water. Urea is not a final oxidation product, and hence contains some energy not fully utilized in the body. The food value of proteins is, therefore, not perfectly expressed in terms of complete oxidation, like that of the carbohydrates, but in terms of *nitrogen content* in addition to *fuel value.*

Carbohydrates.—The foods of this class contain no nitrogen, but belong to the family of saccharids (p. 435). They are the sugars and starches derived mainly from plants, and either eaten pure after separation or taken with the other constituents of the vegetable. Eaten in the dry state, these foods are almost wholly carbohydrates, rice being 79 per cent. starch and 8 per cent. proteins. Allowing 78 per cent. for water in the raw potato, 18.5 per cent. is starch and 2.2 per cent. protein.

Fats.—Derived from both plants and animals are olive and cotton-seed oil, butter, bacon, and tissue fats made up of the non-nitrogenous compounds, stearin, palmitin, olein, and other fats. Being rich in carbon, they are very combustible, and liberate a large amount of heat when oxidized.

Inorganic Salts.—The mineral phosphates, chlorids, carbonates, and sulphates are necessary for the various secretions and promotion of tissue changes, but in great part they circulate in and pass out of the body without much change.

Energy Value of Food.—Excepting the inorganic salts, all the food-stuffs are combustible. By burning them with oxygen in a calorimeter the units of heat set free can be determined and used as an equivalent of nutritive potency. It has been stated (p. 34) that 1 gm. of a carbohydrate yields 4100 small calories or 4.1 Cal. (p. 73). The same heat value is shown by 1 gm. of protein. One

gram of fat gives a much larger amount, viz.: 9300 small calories or 9.3 Cal.

Fats and carbohydrates serve best as sources of ordinary working energy, but to replace the substance of tissue wasted at least an equivalent amount of protein is required in the food. The oxidation products of the fats and carbohydrates are the easily eliminated water and carbon dioxid. On the other hand, the metabolism of nitrogenous substances is attended by the formation of purin bases, uric acid, and other compounds intermediate between protein and its final excrementitious form, urea. These substances above a normal or average mean for the individual are not readily eliminated, and when retained may be the cause of mischief more or less serious. They are especially hurtful when the excretory organs, such as the kidneys, fail to do their share of the work of removing effete matter. It is of prime importance to know, on the one hand, how much food is usually consumed to satisfy the natural craving in a liberal manner and, on the other hand, how little is actually required for the needs of the body under ordinary conditions in the service of health, but not of luxury.

Dietary Standards.—Analysis of the diet of laborers and soldiers of different nationalities has shown that the average daily consumption provides for a total fuel value of over 3000 Cal. The protein average is about 120 gm., containing 19 gm. of nitrogen. The American professional man or sedentary person with moderate work usually takes 100 gm. of protein with fats and carbohydrates, giving energy equivalent to 2700 Cal. The researches of Chittenden upon the diet of professors, athletes, and soldiers, when not taxed by excessive physical or nervous strains, show conclusively that the customary dietaries are in excess of the indispensable minimum and, therefore, in the long run might prove objectionable in a case of inadequate action of the excretory organs, even if the economic aspects be ignored. He found that professional men living regular and care-free lives can maintain a state of nitrogen equilibrium with a daily diet containing 50 gm. of protein and an additional amount of carbohydrate and fat yielding a total energy value of about 2000 Cal. Vigorous health of mind and body continued for months on this diet, containing one-half the amount of protein and two-thirds the calorific power of the standards in use. Athletes free from anxieties, but making heavy demands for muscular work, were in healthy equilibrium on a daily diet of 56 gm. of protein and a total fuel value of about 2500 Cal. The evidence goes to show that all the actual needs of the human body under the regular conditions of a "simple life" can be served on a diet containing much less nitrogen than is customary in the habits and standards of mankind. The best dietary is one in which the vegetable foods predominate and the heavier meats are taken in moderation.

DIGESTION

Mastication.—Digestion begins with the mechanical disintegration of the food in the mouth by chewing, where at the same time it is mixed with saliva. The mass is thus softened, moistened, partly dissolved, and made ready for its propulsion into the stomach. The mixed secretions of the mouth, called *saliva*, contain enzyms which hydrolyze starch and split it into soluble starch, dextrin, maltose, and glucose.

SALIVA

This fluid is a mixture of the secretions of the parotid, submaxillary, sublingual, and buccal glands. It is tasteless, colorless, odorless, viscid, and frothy. It is opalescent and turbid from the floating particles of food, epithelium, and mucous cells. The flow is continuous, but variable, rising in amount by the reflex stimulus of chewing and by the smell and sight of food. The average daily quantity is from 600 to 1500 c.c. (20–50 fl. oz.). Its reaction is faintly alkaline, though sometimes slightly acid after eating; its specific gravity, 1002 to 1008; the proportion of dissolved solids, 5 to 10 parts per thousand.

In 100 parts there are: water, 99.42; mucin and epithelium, 0.22; fats, 0.11; albumin and the two enzyms, salivary amylase ptyalin and maltase, 0.12; salts, 0.13.

The salts include potassium thiocyanate (sulphocyanid), besides the alkaline and earthy chlorids, phosphates, and carbonates. The digestive power of the saliva is in proportion to the quantity of the enzyms. The salivary amylase ptyalin converts cooked starch, through the intermediate stages of soluble starch, dextrin, and erythrodextrin, into maltose and isomaltose (p. 444):

$$\underset{\text{Starch.}}{10(C_6H_{10}O_5)_n} + \underset{\text{Water.}}{4(H_2O)_n} =$$

$$\underset{\text{Maltose.}}{4(C_{12}H_{22}O_{11})_n} + \underset{\text{Achroödextrin.}}{(C_6H_{10}O_5)_n} + \underset{\text{Erythrodextrin.}}{(C_6H_{10}O_5)_n}$$

The other enzym, *maltase*, is in smaller quantity, and converts maltose into glucose (p. 440). Slightly acid or neutral solutions are best suited to the action of these starch-splitting ferments. While they have some activity in the weak carbon acids, this power is lost when the acidity in free HCl reaches that of the gastric juice. The free acid in the active pyloric end, some time after deglutition, destroys part of the amylase, but the salivary fermentation continues first for a considerable period in the gastric fundus, which may be neutral in reaction or weakly acid from acid protein.

Fermenting Power.—By chewing paraffin, a bit of rubber, or glass rod, saliva is made to flow, and collected by spitting into a beaker until 50 c.c. are collected.

Experiment 1.—Having labeled two test-tubes *A* and *B*, place in *A* starch paste and saliva. Put in *B* some saliva, dilute and boil it, then add starch solution and stand both in a water-bath for ten minutes; meanwhile go on with experiments 5, 6, 7, and 8.

Experiment 2.—At the end of ten minutes pour half the contents of *A* into a test-tube containing a drop of HCl and a few drops of iodin solution. If a purple color develop, then starch and dextrin are present; if the color is reddish brown, erythrodextrin and no longer starch; absence of all color indicates absence of both erythrodextrin and starch.

Experiment 3.—If the remaining half of *A* is added to boiling Fehling's solution and a red precipitate falls, a mixture of maltose and glucose is present as the result of fermentation due to ptyalin and glucose.

Experiment 4.—The contents of tube *B*, when treated by tests 2 and 3, show a blue color with iodin and no red precipitate with Fehling's solution. This denotes that boiling the saliva has destroyed its power of digestion and the starch is unchanged.

Chemical Properties.—While waiting for the fermentation tests, a further flow of saliva may be caused and the reaction taken with litmus paper.

Experiment 5.—On addition of acetic acid to dilute saliva a precipitate shows mucin.

Experiment 6.—Boiling with strong nitric acid gives a yellow color, which deepens if ammonia be added. This denotes a protein.

Experiment 7.—A drop of nitric acid and silver nitrate shows the chlorids by a white precipitate.

Experiment 8.—Ferric chlorid turns the saliva red from the presence of a sulphocyanate with a trace of hydrochloric acid.

Experiment 9.—A gelatine capsule containing 3 gr. (0.2 gm.) of potassium iodid is swallowed and the mouth quickly rinsed with water and the saliva tested. At intervals of two minutes it is tested again for the potassium iodid, by adding to it in a test-tube some cold starch paste and a drop of yellow (nitroso-) nitric acid. A blue color denotes the excretion of potassium iodid by the salivary glands.

GASTRIC CONTENTS

Gastric Juice.—When food enters the stomach, or is merely presented to the senses, or well chewed before swallowing, there is secreted a fluid called the *gastric juice*. If free from food particles, it is thin, clear, or faintly cloudy, pale yellow, with a

strongly acid reaction and a specific gravity of 1002 to 1003. In a day the amount poured out will vary between 3 and 6 pt., part of which is absorbed with the digested product while fresh portions are being secreted. By reflex action the production of gastric juice is strongly stimulated by the taste of food or bitter substances in the mouth. The juice which is secreted by psychic or "appetite" stimulus is most important, inaugurating gastric digestion, the first products of which, when absorbed, in their turn stimulate secretion by a reflex circuit including excitable nerve-endings in the mucous membrane of the stomach. To excite the secretion of this psychic juice, eating must be done with attention and relish. Water alone introduced into the stomach will cause some flow, but food will increase it greatly. A free secretion does not take place until there has been some absorption; hence the advantage of having soup as the first course of a meal. When pure and free from residues of food, the acid reaction is chiefly, if not wholly, due to hydrochloric acid, about 0.2 or 0.3 part per cent. The protein material contained in fresh gastric juice is due to a little mucin and two enzyms, *pepsin* and *rennin.*

Average composition of gastric juice.	Per cent.
Water	99.44
Solids, as tabulated below	0.56
Organic substances (pepsin and peptones)	0.32
Free hydrochloric acid	0.25
Sodium, potassium, and calcium chlorids	0.21
Calcium, magnesium, and ferric phosphates	0.02

Pepsin.—A characteristic property of the pepsin is its power of converting proteins into dissolved proteoses and peptones in an acid, but not in a neutral or alkaline medium. The protein swells and clears up before it dissolves. The albumin of hard-boiled egg cut into disks 1 mm. thick is not altered by dilute hydrochloric acid when immersed in it for several hours at the temperature of the body. If, however, pepsin has been present, the edges become clear, transparent, and swollen, and the albumin dissolves. On the other hand, pepsin alone has no action on proteins, the acid, too, being essential (see p. 562).

Pepsinum, U. S. P., is the enzym as obtained from the glandular layer of the fresh stomach of the hog. It occurs in yellowish white scales or powder, having a slightly acid taste. It is soluble in 50 parts of water; more soluble in water acidulated with hydrochloric acid. If that acid is present in greater strength than 0.5 per cent., the proteolytic activity is checked and destroyed. It is incompatible with pancreatin, destroying it if the mixture be acid; if the solution be neutral or alkaline, the pancreatin destroys the pepsin.

Rennin, or chymosin, is the enzym which is characterized by

coagulating the casein of milk. It may be absent in carcinoma, chronic catarrh, and atrophy of the membrane of the stomach.

Chyme is the pulpy mass into which the food is converted in the stomach by the action of the gastric juice and saliva. It is acid in reaction and contains the transformation products of digestion of carbohydrates and proteins, mixed with much-changed but undigested matter which remains to be digested in the intestines. The albuminous foods are prepared in the stomach for a final digestive process of the intestines.

A swollen and slippery change marks partial digestion of meat, muscle, and cartilage. The combination of pepsin and rennin curdles milk either in large lumps of cheese or smaller flocculi distributed through the mass. Bread is pulpified, though other vegetable foods, such as potatoes, may be found in distinct morsels. Part of the starch taken is converted into dextrin and sugar while digesting in the quiet fundus.

It is probable that the fundus secretes a *lipase* capable of splitting emulsified fat.

In the antrum pylori is secreted a *hormone* or *secretin*, which on absorption stimulates the secretion of the peptic glands. Another gastric hormone stimulates peristalsis of the intestines.

CLINICAL EXAMINATION

The scope of this section does not include all the physiologic and pathologic relations of the stomach contents, but only such as have clinical value. The range of the casual examination may be summarized in the following procedures, which are enlarged upon later on:

Filter the gastric contents and use the filtrate.

(*A*) Test acidity with litmus paper; it may be normal, superacid, subacid, anacid.

(*B*) Find the acid when not combined. For free acid use Congo red, or tropeolin oo. To tell the kind of acid: For hydrochloric acid use Töpfer's reagent, which shows 0.02 per 1000; or Günzburg's reagent, which is delicate for 0.05 per 1000; or Boas' reagent, which has the same delicacy as Günzburg's (p. 558).

For lactic acid use Uffelmann's reagent, which is delicate for 0.1 per 1000 (p. 561).

(*C*) Determine total acidity: Titrate 10 c.c. of filtrate to which has been added phenolphthalein (1 per cent. alcoholic solution), 2 drops, with a decinormal solution of caustic soda (4 gm. to 1 L.)—1 c.c. of this solution = 0.003646 gm. of HCl or 0.009 gm. of lactic acid.

Hydrochloric acid is normal at end of first hour in parts 1.5 to

2 per 1000 (0.15 to 0.2 per cent.); or at end of third or fourth hour in parts 2.3 to 3 per 1000 (0.23 to 0.3 per cent.).

Gross inspection of vomited matters or stomach contents consists in noting the presence or absence of—(1) food particles and whether fresh or old; also the progress of digestion. (2) Blood, whether bright or coffee-ground color. (3) Mucus. (4) Odor. (5) Apparent amount of gastric juice, keeping in mind that after digestion is complete the secretion of gastric juice should cease. Continuous secretion is abnormal and is known as *parasecretion* (Ewald).

Microscopic Examination.—Here are to be looked for food fragments, starch granules, plant cells, muscle-fibers, connective tissues, epithelial cells from mouth and esophagus, cylindric cells from the stomach, leukocytes, red blood-cells, pus-cells, parasites, and low organisms, as yeast cells, mold fungi, sarcinæ, bacteria.

Gastric Acids.—In the first stage of digestion there may be a predominance of lactic acid developed in the fermentation of the carbohydrates by the *Bacterium lactis;* in the second stage both lactic and hydrochloric acids occur; in the third stage hydrochloric acid has checked the formation of lactic acid, and the acid reaction now is due almost exclusively to hydrochloric acid. Decomposition of the stomach contents may be prevented for some time by the antifermentative action of the hydrochloric acid. If the acid be neutralized, the chyme ferments produce lactic, acetic, and butyric acids. To various disease germs hydrochloric acid is an antiseptic when present in normal proportions, killing the cholera germ and the micrococci of pus. It is one of our chemical defenses against disease, but it does not, however, destroy the bacillus of tuberculosis nor that of anthrax. It has another action in promoting the solution of the calcium and magnesium salts which are required for the growth of bone.

The **quantity of hydrochloric acid** bears an important relation to certain pathologic states, and must be determined so as to aid in diagnosis. When there is an excess, the symptom is called *hyperchlorhydria;* when it is deficient, *hypochlorhydria;* when absent, *achlorhydria*, and when normal, *euchlorhydria.*

It is not only necessary to ascertain the degree of acidity, but also the nature of the acid or acids occurring. This may be done by coloring substances which give characteristic reactions with hydrochloric acid in very minute quantities, but not with lactic acid or any organic acid in any degree of concentration found in the stomach. It is conceded that these reactions are not sufficiently distinctive for exact studies, but for comparative studies and clinical purposes they are accurate enough, and serve the purposes better than more exact methods, too difficult for the clinician. To simplify the study and provide a definite point in

digestion for comparison of data, it is customary to limit the inquiry to the contents of the stomach one hour after a very simple meal. At this time the greater part has not passed through the pylorus, the secretion of hydrochloric acid has about reached its height, and only a trace of lactic acid has been left unabsorbed. All the components of an ordinary mixed meal in an easily digestible form are represented in the *test-breakfast* of Ewald.

The **test-meal** is given in the morning as a breakfast. It may be given at another time, provided the stomach is empty or has been washed out as a preliminary measure. It consists of an ordinary roll of dry bread, weighing about 35 gm. (9 dr.), and 300 c.c. or about 10 fl. oz. of hot water or weak tea, taken without cream or sugar. In one hour this will be liquefied, and 1 or 2 fl. oz. (30–60 c.c.) can be easily expressed through a tube.

The **stomach-tube** offering the most advantages is a flexible one of soft rubber, smooth on the surface and also at the round opening near the end that enters the stomach. It should be long enough to enter the stomach and leave enough tubing outside the mouth to reach a receptacle. This outer end may have a funnel attachment or an elastic bulb to start the flow of the gastric contents until the tube is full enough for siphon action. In an emergency a *Davidson syringe* or a *Politzer bag* will serve to start the flow.

The patient sits erect in a chair or on the edge of a bed, with the receptacle near by. The tube, wet in hot water, is passed back to the throat and the patient makes an effort at swallowing. Assisting deglutition, it readily passes into the stomach. Evacuation may occur at once, without effort, simply by depressing the external end of the tube so as to make a siphon. Pressure over the abdomen, in the recumbent posture, while the patient coughs or bears down, is of material help. When 10 fl. oz. (300 c.c.) of water or tea have been given, about $1\frac{1}{2}$ fl. oz. (45 c.c.) of fluid should be obtained by the tube. Filtration yields a clear solution for the application of the tests. Should there be much gagging from nervousness or pharyngeal irritability, a spray of cocain (4 per cent.) will prepare the way for the tube.

Dangers to be Avoided.—Ordinarily, the use of the stomach-tube is an easy and safe procedure, but it is contraindicated in acute fevers, emphysema with bronchitis, organic heart disease, aortic aneurysm, the hemorrhagic diathesis, corrosive poisoning threatening perforation, and soft carcinoma of the stomach.

The **specimen** from the test-meal, when examined by the naked eye, need not be searched for all of the numerous objects referred to above. If the contents be normal, they will be composed of about 40 c.c. of a whitish fluid, some mucus, and a sediment of

bread débris. After filtration the fluid should contain hydrochloric acid, pepsin, rennin, peptone, and mineral salts.

The **chemical examination** should begin by the use of litmus paper to determine the reaction. Normally, blue litmus will be reddened; if it be unaffected, then there is a condition known as *Anacidity* (Plate 5, Fig. 1).

The next step should be to determine if the acidity be due to free acid, to acid salts, or acid proteins. Litmus paper does not discriminate these. A very convenient test is made with the anilin colors, Congo red or tropeolin oo (dimethyl orange), both of which react to minute quantities of free hydrochloric acid, but are unaffected by acid salts or by the organic acids in the amounts present after the test-meal. A positive reaction with either serves for ordinary purposes.

Congo-red Test.—Upon Congo-red paper place a drop of the gastric contents. A deep blue spot appears if free hydrochloric acid be present—as much as 0.005 per cent. (the normal amount is 0.25 per cent.). A violet spot or a blue ring only around the wet place may be produced by any free acid, either a trace of hydrochloric acid or some organic acid—lactic, butyric, or acetic (Plate 5, Fig. 2).

Tropeolin (Dimethyl-orange) Test.—The test is made with saturated alcoholic solution of pure tropeolin (oo). With this solution wet some white filtering-paper and then let it dry. Touch the prepared paper with a drop of the gastric contents. When hydrochloric acid is present to 0.02 per cent., a dark reddish brown spot appears, which changes to lilac or bluish if gently heated on a watch-glass. The organic acids as found in the gastric contents do not have any effect. In larger amounts they make a faint brown stain which does not show a lilac color when heated.

The Liquid Method of performing this test is to put 2 or 3 drops of gastric fluid in a porcelain dish, spread them, and evaporate almost to dryness. Touch this residue with a drop of tropeolin solution and gently warm. A bluish spot indicates free hydrochloric acid—at least 0.02 per cent. No organic acid gives the blue color.

The most delicate tests for distinguishing hydrochloric acid are *Töpfer's dimethylamino-azobenzol*, *Günzburg's phloroglucinvanillin*, and *Boas' resorcinol solutions*. They do not respond to the organic acids as found in the stomach after a test-meal.

Töpfer's solution is made by dissolving 0.5 gm. of dimethylamino-azobenzol in 100 c.c. of alcohol. A drop of the gastric juice, even when unfiltered, will turn a drop of this yellow solution to a cherry-red color. Organic acids affect it only when present to 0.5

PLATE 5.

THE MOST IMPORTANT COLOR-REACTIONS OF THE GASTRIC JUICE.

FIG. 1, *a* and *b*. When the gastric juice reddens blue *litmus-paper* (*b*)—that is, exhibits an acid reaction—it may contain: free hydrochloric acid, lactic acid, and other organic acids, acid salts.

FIG. 2, *a* and *b*. If red *Congo-paper* is stained bluish-black (*b*) by the gastric juice, only free hydrochloric acid or lactic acid is present.

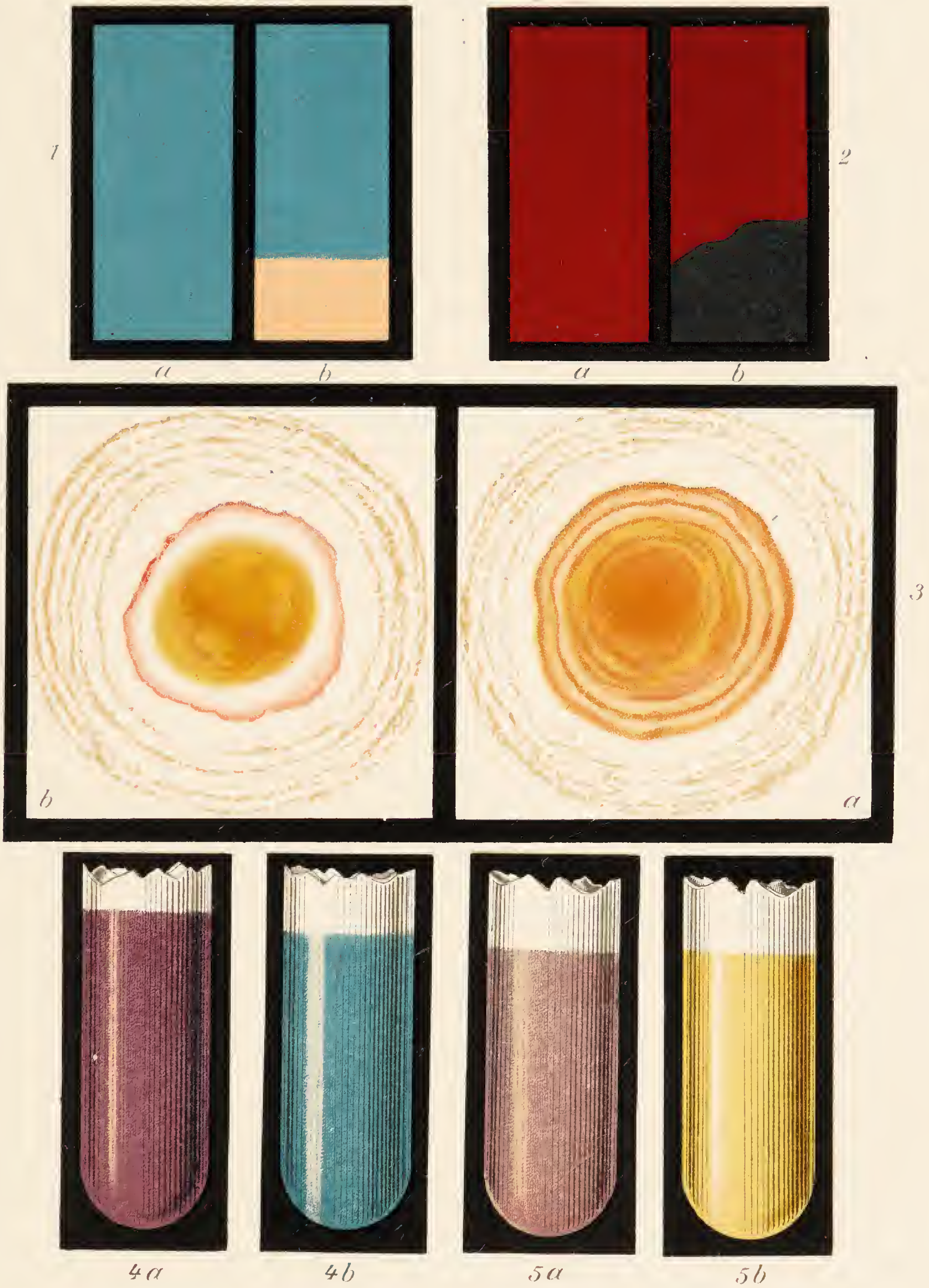
FIG. 3, *a* and *b*. If upon evaporation of the gastric juice in a porcelain dish, to which a few drops of *phloroglucin-vanillin solution* have been added, a distinct red ring appears, free hydrochloric acid is present; if the residue remains yellow, no free hydrochloric acid is present (anacidity).

FIG. 4, *a* and *b*. If the gastric juice contains hydrochloric acid, the violet color of a dilute *methyl-violet solution* is converted into blue (*b*). (This test is not absolutely reliable.)

FIG. 5, *a* and *b*. If the gastric juice contains lactic acid, it will change the violet color of *Uffelmann's reagent* (1% solution of carbolic acid, with 2 drops of iron chlorid) into a distinct yellow (*b*). This test is more reliable if performed with an ethereal extract of the gastric juice (lactic acid being soluble in ether).

(JAKOB.)

PLATE 5.



ESTIMATION OF TOTAL ACIDITY, ACID PROTEINS, FREE HCl, AND ORGANIC ACIDS

The procedure generally adopted is *acidimetry*, operating with the same standard alkali solution upon the acid gastric contents in three different dishes, each with a different indicator, to make three different reports:

Total Acidity.—It has been stated above that hydrochloric acid is an antiferment. If detected in the gastric contents one hour after a test-breakfast, it may be assumed that there is very little organic acid present. After ascertaining the presence of hydrochloric acid and absence of lactic acid, to determine the *total acidity* is practically to estimate the amount of hydrochloric acid present. A more thorough study is needed when the organic acids are detected.

The reagent required is *decinormal sodium hydroxid*, each cubic centimeter containing 0.004 gm. of NaOH, which neutralizes 0.00364 gm. of HCl. This solution should be carefully standardized after the method given on p. 125. In the first dish the indicator is phenolphthalein, 1 per cent. alcoholic solution, which is kept colorless by all free acids and acid proteins, but turns red by alkalis (Plate 6, A, A′).

Method.—To 10 c.c. or 5 c.c. of the filtered gastric fluid in a dish or beaker 2 drops of a solution of phenolphthalein are added. A buret is charged with the decinormal soda solution, and a few drops at a time are run into the liquid until a deep red color persists of the same intensity. If 10 c.c. of the gastric contents have been used and the amount of hydrochloric acid be normal, it will require from 4 to 5 c.c. of the solution to change the color. One cubic centimeter will neutralize 0.00364 gm. of HCl; if 3 c.c. have been required, then the acidity is calculated thus: $3 \times 0.00364 = 0.01092$ of HCl. To get percentage: $0.01092 \times 10 = 0.1092$ per cent. of HCl. If 5 c.c. of gastric liquid were used, then $0.1092 \times 20 = 0.2184$ per cent. of HCl.

The acidity is expressed for clinical purposes by the number of cubic centimeters of decinormal sodium hydroxid which are required to neutralize 100 c.c. of the stomach liquid. To get this when the operation has been performed on 10 c.c., multiply the reading by 10. Acidity of 45 per cent. would then mean that 100 c.c. of the gastric liquid required 45 c.c. of decinormal sodium hydroxid to neutralize it. It would be spoken of as "total acidity, 45 degrees," in terms of NaOH. The acidity of normal gastric contents varies between 40 and 60 degrees.

Free Acids not Combined with Proteins.—When phenolphthalein is the indicator, the reaction is caused by all free acids and by loosely combined acids. If we wish to estimate the free

acids, but not the acid protein or loosely combined acid, we must use another indicator.

Alizarin (sodium alizarin monosulphonate) in a 1 per cent. aqueous solution is acted upon by all acids except the acid proteins. The difference between the two numbers, *total acidity* and *acids not acid protein*, will be the degree or number representing the *acid protein*, or loosely combined acid.

Procedure.—Add 2 drops of alizarin sulphonate as an indicator to 10 c.c. of stomach contents in dish No. 2, and from a buret run into it slowly the decinormal sodium hydroxid until a pure violet color appears untinted by red. The combined acid does not figure in the color changes of this dye[1] (Plate 6, B, B′).

Acid Protein.—If 2 c.c. of soda solution were required to reach the clear violet in the last titration and 3 c.c. were required for *total acidity*, then $3-2=1$ c.c., required for loosely combined acid; 1 c.c. $\times 10 = 10$ c.c., representing degrees of combined acid in 100 of gastric contents.

Free Hydrochloric Acid.—As alizarin indicates all the free acids, to ascertain the amount of free HCl, as distinguished from the organic acids, another indicator must be used which is affected by the hydrochloric acid only. This is the valuable property of *Töpfer's reagent*, dimethylamido-azobenzol, in 0.5 per cent. alcoholic solution.

Method.—Having filled the buret with decinormal sodium hydroxid, place in dish No. 3 10 c.c. of gastric contents and 3 drops of Töpfer's indicator, which is yellow. If it turn red, then HCl is present, and we must run in the sodium hydroxid slowly until the yellow color is restored. If this be done in the proportion of 1 c.c. for the 10 c.c. of gastric contents used, then for 100 it would be $1 \times 10 = 10$ c.c. of decinormal sodium hydroxid to neutralize the free HCl in 100 c.c. of gastric contents, or 10 degrees. To calculate percentage in weight of HCl: $10 \times 0.00365 = 0.0365$ gm. in 100 c.c. of gastric contents (Plate 6, C, C′).

Organic acids and **acid salts** are estimated by subtracting the degrees of *free HCl* from *all acids except acid proteins*. In the case above given the calculation would be 20 degrees less 10 degrees = 10 degrees for organic acids and acid salts.

Detection of Lactic, Acetic, and Butyric Acids.—Lactic Acid (*Kelling's Test*).—To 5 c.c. of gastric contents add 50 to 100

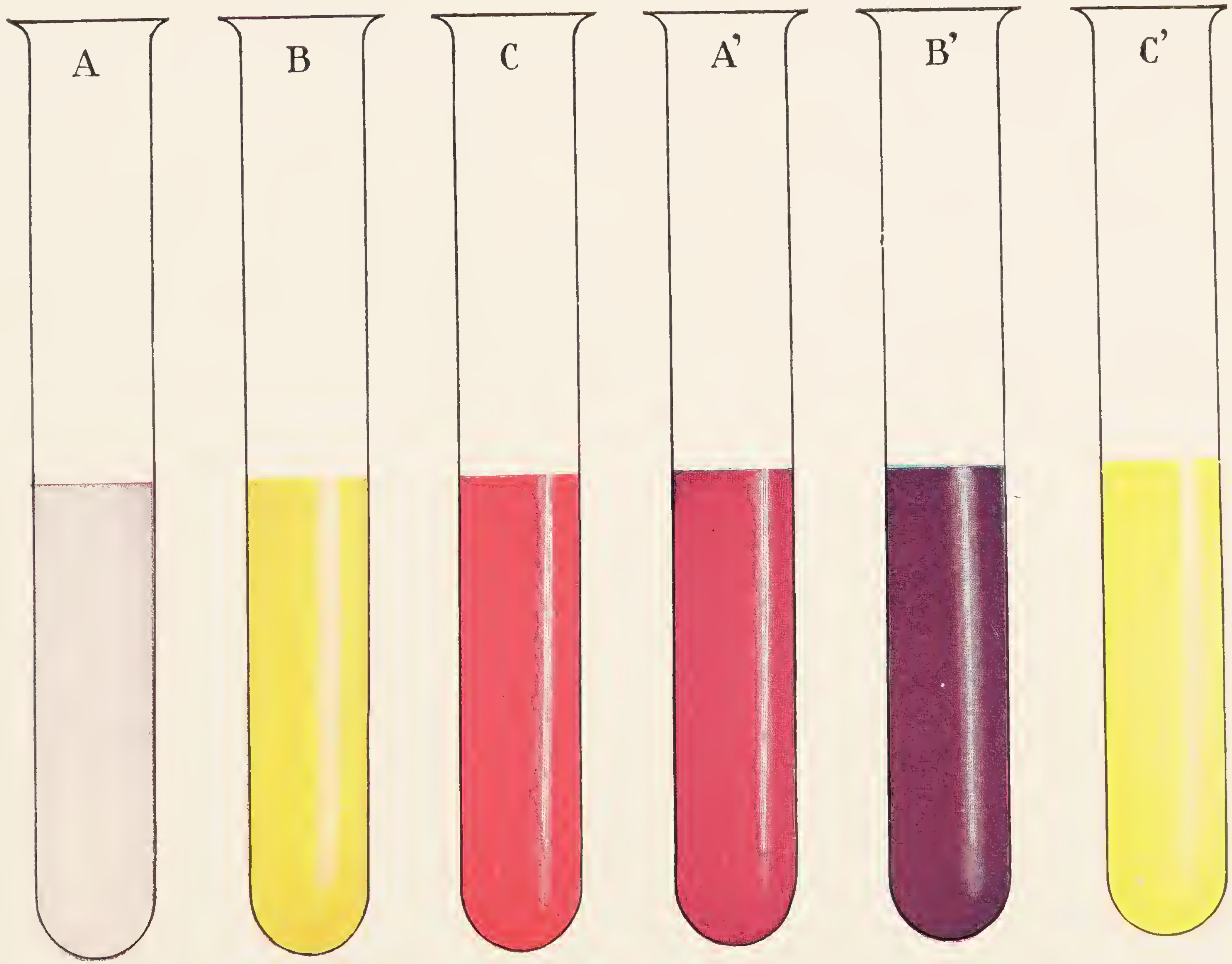
[1] Töpfer recommends the following preliminary steps to familiarize the eye with the color required in the reaction with alizarin sulphonate:

(*a*) To 5 c.c. of distilled water add a few drops of alizarin solution. A clear yellow color results. This varies somewhat, at times a clear red color resulting.

(*b*) To 5 c.c. of a 1 per cent. solution of disodium phosphate add a few drops of the alizarin solution. A reddish color with a tinge of violet results.

(*c*) To 5 c.c. of a 1 per cent. solution of sodium carbonate add a few drops of alizarin solution. A clear violet tint—the reaction to be recognized in the test—results.

PLATE 6.



A. Gastric fluid to which a 1 per cent. solution of phenolphthalein has been added.
B. Gastric fluid to which a 1 per cent. solution of alizarin has been added.
C. Gastric fluid to which a 0.5 per cent. solution of dimethylamido-azobenzol has been added.
A'. A after titration with a decinormal solution of sodium hydrate.
B'. B after titration with a decinormal solution of sodium hydrate.
C'. C after titration with a decinormal solution of sodium hydrate.

(BOSTON.)

c.c. of water, so that the fluid shall not be yellow. Treat with 2 drops of a 5 per cent. aqueous solution of ferric chlorid and hold to the light. A distinct greenish yellow color is evidence of lactic acid having formed ferric lactate. The presence of a small amount of hydrochloric acid has no influence on this reaction, which is due to the organic salt being undissociated.

It is not interfered with by the organic substances of the gastric contents, which may make Uffelmann's test useless.

Carboloferric or Uffelmann's Test.—Prepare Uffelmann's reagent freshly by mixing 1 drop of a dilute solution of ferric chlorid (U. S. P.) with 2½ fl. dr. (10 c.c.) of a 4 per cent. solution of carbolic acid and 5 fl. dr. (20 c.c.) of water. When first made, the reagent has an amethystine-blue color (Plate 5, Figs. 5a and 5b′).

Method.—Equal parts of Uffelmann's reagent and filtered gastric contents are mixed, and if more than 0.01 per cent. of lactic acid be present, the color changes to canary yellow or greenish yellow. The other acids may discharge the blue color, but not develop the yellow if the very unusual amount of 0.3 per cent. be present.

Fallacies may occur from the previous color of the gastric fluid or the presence of glucose, phosphates, etc., giving color reaction that masks the lactic acid. A relatively pure and concentrated sample can be obtained by making an *ethereal extract.* Fill a test-tube three-fourths full with the gastric fluid, add ether, and shake vigorously some minutes. Stand aside till the ether separates at the top with the lactic acid in it. Then pour off the ether into a porcelain dish. Repeat with fresh ether three times. All the ether is then evaporated, but not over an open flame. To the residue add a few drops of water and then Kelling's ferric chlorid or Uffelmann's carboloferric reagent. If the fluid does not turn yellow, there is no lactic acid.

Acetic and Butyric Acids.—The above ethereal residue reveals the presence of any acid by the reaction, and the volatile acetic and butyric acids by their odor.

Butyric Acid.—If a portion of the ethereal extract be diluted and a piece of calcium chlorid added, the light butyric acid will float like oil globules on the saline solution below.

Acetic Acid.—A portion of the ethereal extract is carefully neutralized by sodium or potassium hydroxid, 1 drop of solution of ferric chlorid is added. Acetic acid forms red ferric acetate, which on boiling precipitates as the brownish basic salt.

Import in Diagnosis.—It has been found that 85 per cent. of patients showing a marked amount of lactic acid have malignant changes in the wall of the stomach. This lactic acid appears simultaneously with the disappearance of the hydrochloric acid

and is therefore attributed to fermentative changes in the food which would have been prevented if the hydrochloric acid had been normal in amount (p. 554).

GASTRIC DIGESTION TESTS

The power of proteolysis possessed by the gastric contents is practically dependent on the presence of pepsin. To test that power is to prove that the ferment is active, provided always that provision is made for the acidity of the medium.

Pepsin.—Fibrin is easily digested and is preferred to albumin, though it is not so easily obtained. Let fresh blood stand till it clots. The clot washed in water at a running tap loses color and is called *fibrin*. It can be kept in glycerin and washed before use. Into a test-tube or watch-glass containing 2 dr. or more of filtered gastric contents put 2 drops of hydrochloric acid and a piece of fibrin. Stand aside for a half hour or more at a temperature of 40° C. (104° F.). If pepsin be present, the fibrin will be smaller by partial solution. For practice the student can make an artificial gastric juice by dissolving 1½ gr. of pepsin in 1 fl. oz. of water and adding 5 drops of hydrochloric acid.

Estimation of Pepsin Strength.—Cut hard-boiled white of egg into pieces $\frac{1}{25}$ in. (1 mm.) thick, and punch out disks $\frac{2}{5}$ in. (10 mm.) in diameter. Four test-tubes are labeled by clasping to the necks with rubber bands pieces of paper numbered from 1 to 4. A memorandum must be kept to the effect that there is added: to the first 2½ fl. dr. (10 c.c.) of the clear filtrate of gastric contents; to the second, the clear filtrate + HCl, enough to make 0.3 to 0.5 per cent. solution, filtrate, 2½ dr. (10 c.c.), HCl, 2 drops; to the third, the clear filtrate + pepsin in scales, filtrate, 2½ dr. (10 c.c.), pepsin, 3 to 7 gr.; to the fourth, the clear filtrate + HCl + pepsin as in 2 and 3 above; place all in a warmer at 40° C. (104° F.) and watch the progress of digestion for two hours.

If pepsin and acid be present in normal amount, the disks will all dissolve in one to two hours. If the acid be deficient, then solution will not occur in samples 1 and 3, but will occur in 2 and 4. If pepsin be deficient, digestion will not occur in 1 and 2 as rapidly as in 3 and 4.

Clinical Import.—Absence of pepsin is rare even in serious disease of the stomach. Failure in gastric digestion is seldom due to the lack of it. If the flakes of albumin digest without adding hydrochloric acid, it does not prove a normal state of things, as digestion is possible by the presence of lactic acid alone, though the condition is not a healthy one.

Rennet Ferment, or Rennin.—Take a small amount, 2½ dr., of neutralized filtrate and add an equal amount of neutralized

boiled milk. Place in warm chamber at 37.7° C. (100° F.) for ten to fifteen minutes—the milk will curdle.

Digestion of Albumin.—It is seldom of any value to carry the investigation further, but, if desired, tests can be applied to determine the progress of the digestion of albumin, as follows:

(1) **Heat** the filtrate of stomach contents to boiling:

(*a*) Coagulating indicates either albumin or syntonin.

(*b*) No coagulation implies that there may be propeptone (this is precipitated by cold and redissolved by heat) or peptone (heat has absolutely no influence upon it).

(*c*) If the filtrate be acid, neutralize a fresh portion and heat. A precipitate now indicates syntonin. Filter and use filtrate as in No. 3, below.

(2) **Biuret Reaction.**—Heat the filtrate with caustic potash, and add dilute solution of cupric sulphate, drop by drop, from pipet. Note the reaction.

(*a*) If an intense purple-red color appear, it indicates propeptone or peptone.

(*b*) If a bluish-violet color appear, there may be albumin or syntonin (Plate 8, Fig. 7).

(3) From *c* of No. 1, above, take the filtrate and treat with acetic acid and potassium ferrocyanid. If there be no precipitate and the biuret be positive, then peptone is present. Confirm by tannin the salts of heavy metals (mercuric chlorid, potassic iodid, etc.), or phosphotungstic acid, all of which precipitate it.

Motor Function of the Stomach.—The **lavage test** is used to determine if there be pyloric stenosis or other condition of the stomach, such as atony or dilatation, which prevents the propulsion of the contents on to the duodenum. *Method:* Give 10 raisins or stewed prunes at 10 P.M. and wash out the stomach with water at 9 A.M. next day. Seeds and vegetable tissue should not be found in seven hours. In defective motility they are sometimes seen even after two or three days.

Peptic Activity.—**Sahli's desmoid test** is based upon the observation that raw catgut is digested in the gastric, but not in the pancreatic juice. *Method:* After the mid-day meal give a soft pill of methylene-blue 0.05 gm. ($\frac{3}{4}$ gr.) and Ex. glycyrrhizæ q. s. to make a pill $\frac{1}{6}$ inch in diameter. The pill is wrapped close with a thin sheet of rubber 2 c.c. in diameter and tied tight with 3 turns of raw catgut No. 00, previously softened by soaking over night. The pill should sink in water and not color it. Examine the urine passed at 7 P.M. and again at 9 A.M. next day. In health, the first bluish-green tint appears seven hours after taking the pill. If decided color shows inside of twenty hours the peptic activity is probably good.

PANCREATIC JUICE

The changes in the alimentary bolus, due to insalivation and gastric digestion, may be regarded to a large extent as preliminary to the digestive processes of the intestines. Those earlier alterations may be entirely canceled in some animals without material differences in the products of digestion. The pancreas is the only digestive gland in many animals, and is found in all that have an alimentary canal. In the higher vertebrates its destruction means death. When the acid contents of the stomach pass into the duodemum, a substance is set free by the duodenal glands belonging to the class of chemical messengers or *hormones* called *secretin*, which enters the blood and, passing to the pancreas, starts secretion there. Reflex excitation of the pancreas, liver, and intestinal glands results in a flow of alkaline secretions, which put a stop to gastric digestion by destroying the reaction of the chyme and substituting one favorable to the activity of the new enzyms that are destined to carry the alimentary bolus through complex chemical changes to the end-products. Beside the *internal* secretion of the pancreas, which is taken up by the blood and serves by a retarding *hormone* to regulate the sugar production from glycogen in the liver and from protein metabolism in the muscles, there is the *external digestive* fluid elaborated by the gland cells from the blood and lymph and poured into the intestines. The highest rate of flow occurs about three hours after eating, but there is another rise two hours later.

The total amount is about 22 c.c. per kilo of body-weight of the animal. In man the daily estimates vary between 150 c.c. and 500 c.c. ($\frac{1}{4}$–1 pint). It is a strongly alkaline fluid, clear, colorless, odorless, viscid, with a specific gravity of 1008. The secretion in the dog contains about 1 per cent. of solids, two-thirds of which is composed of albumins, peptones, and ferments, and the other one-third of mineral salts and such organic matter as leucin, fat, and soaps. The salts are equal in alkalinity to 3 parts per 1000 of sodium carbonate. The ferments include at least 4 enzyms that are well defined, and two others about which little is known. In the first group are: (1) *Amylopsin* (pancreatic diastase, amylase), starch-splitting. (2) *Trypsin* (protease), protein-splitting. (3) *Steapsin* (lipase), fat-splitting. (4) *Pancreatic rennin*, milk-curdling. In the little-known group are *erepsin* and *lactase*.

The relative amounts are the results of a response to the reflex stimulus of food. A diet rich in starches causes a rise in the proportion of amylopsin; one rich in fats, an increase in steapsin.

Pancreatic amylase (*amylopsin*) is an amylase acting like the salivary amylase, though with greater energy. All starchy food that passes the stomach unchanged is at once converted by this enzym into dextrin and maltose.

Trypsin is a proteolytic enzym formed from the zymogen *trypsinogen* secreted by the gland cells by the action of an enzym of the intestinal juice called *enterokinase.* It is soluble in water, but not in alcohol. When acidulated and boiled, trypsin loses its enzymic power and breaks up into an albuminous coagulum and a peptone. Its best temperature for work is 40° C.(104° F.). Traces of free mineral acid inhibit its action. In alkaline solution it dissolves its proteins, fibrin, albumin, globulin, and gelatin much better than the pepsin of the gastric juice, and breaks them up more completely. When the alkali albumin changes to the dissolved albumoses, these change, first, to peptones, and later, by the aid of another enzym, *erepsin,* to the amino-acids (leucin, tyrosin, aspartic acid, the sulphur compound, cystin, etc.), and the hexon bases (lysin, arginin, and histidin). At one of the intermediate stages, after the formation of albumose, tryptophan is produced. This is skatol-amino-acetic acid. It is regarded as the mother-substance of the aromatic products indol and skatol. Its presence is shown by the Adamkiewicz reaction (p. 506) and by the violet color produced when the protein mixture is acidified with acetic acid and treated with two and a half times its volume of bromin-water.

Steapsin has the property of hydrolyzing and splitting fats into glycerin and fatty acids, which change to soap by union with the sodium carbonate of the intestinal juices. It is probable that this reaction extends to the separation of only a part of the acid, which, when saponified, aids in the emulsification and absorption of the remainder. Another view is that the fat is all split first and passes through the intestinal walls as soap and glycerin, to be built up again by cell action to molecular fat on the other side.

Pancreatinum, U. S. P., is a mixture of the enzyms obtained from the fresh pancreas of the hog or ox, and consisting of amylopsin, trypsin, and steapsin. It is a cream-colored powder with a faint odor and a meat-like taste. It is slowly soluble in water. It is rendered inert by more than a trace of mineral acid, by excess of alkalis, and by pepsin in solution.

Fermenting Power.—The most powerful and active fermentation of the pancreatic juice is that of conversion of starch into maltose. It will act even on unboiled starch. For this test an extract may be made by bruising finely minced fresh pancreas with glycerin.

Experiment 1.—For the proteolytic fermentation, 1 per cent. solution of sodium carbonate is put in a test-tube and a small amount of the pancreatic glycerin is added. Put some of it in two test-tubes labeled *A* and *B*. To *A* add a piece of fibrin, and after boiling the contents of *B* put in it a piece of fibrin. Stand both in a water-bath for thirty minutes. The fibrin in *A* will look

eroded, not swelled as by gastric juice, and when tested by the biuret reaction gives the pink color due to peptone. Tube *C* shows no change in the fibrin, indicating that boiling has been fatal to the ferment.

Experiment 2.—Into a test-tube labeled *C* put starch paste and a few drops of the glycerin extract of pancreas, without soda, and stand in a water-bath for ten minutes. Take out a few drops and test every minute with iodin on a white dish. When the blue reaction ceases, test with Fehling's solution; maltose will be shown by the red precipitate.

Experiment 3.—As glycerin does not dissolve steapsin, the pancreatic glycerin will not serve to show the fat-splitting fermentation. For this it is best to use a small piece of fresh pancreas or an extract made by digesting fresh pancreas, minced, in 4 parts of dilute alcohol (1 of alcohol to 4 of water) for five days and then filtering. Into a test-tube labeled *D* put milk and blue litmus with a piece of fresh pancreas and stand in a water-bath for thirty minutes. The liberation of the fatty acids is shown by the litmus turning red.

Experiment 4.—If the pancreatic glycerin with sodium carbonate solution is shaken with olive oil, an emulsion is formed.

BILE

The liver secretes bile continuously, but pours it into the duodenum according to the nature and amount of food. The flow increases when food first arrives in the duodenum, and a second wave rises some hours later, when the digestive products in the blood stimulate the hepatic cells. It is yellow to green in color, alkaline in reaction, and of a specific gravity between 1010 and 1040. The daily amount in man varies from 500 to 1000 c.c. (1–2 pt.).

In 100 parts about 14 are solids, the rest being water. Of the solids, sodium glycocholate and taurocholate make 9 per cent.; cholesterin, lecithin, and fat, 1.18; mucinoid material and pigment, 3; inorganic salts, 0.82. The characteristic salts are sodium compounds with complex amino-acids—glycocholic and taurocholic. *Glycocholic* acid in the intestine, or by the action of dilute alkalis and acids, hydrolyzes and splits into glycin (amino-acetic acid) and cholalic acid; thus:

$$\underset{\text{Glycocholic acid.}}{C_{26}H_{43}NO_6} + H_2O = \underset{\text{Amino-acetic acid.}}{CH_2 \,.\, NH_2 \,.\, COOH} + \underset{\text{Cholalic acid.}}{C_{24}H_{40}O_5}$$

Taurocholic acid contains sulphur, and splits after hydrolysis into taurin (amino-ethyl-sulphonic acid) and cholalic acid; thus:

$$\underset{\text{Taurocholic acid.}}{C_{26}H_{45}NO_7S} + H_2O = \underset{\text{Taurin.}}{C_2H_4 \,.\, NH_2 \,.\, HSO_3} + \underset{\text{Cholalic acid.}}{C_{24}H_{40}O_5}$$

Pettenkofer's reaction (p. 569) is obtained by mixing the bile salts with cane-sugar and sulphuric acid or with furfurol direct. A bright red color appears and later changes to violet.

Cholesterol is present in the nerve tissues, the blood-corpuscles, semen, pus, etc. It is a constituent of the fat obtained from sheep's wool (*lanolin*). Only a small quantity is contained in normal bile, but at times it becomes excessive and forms concretions known as gall-stones. Though, like fats, it is soluble in ether, it is not a true saponifiable fat, but an alcohol with the formula $C_{27}H_{45}OH$. Part of the wool-fat, *adeps lanæ*, U. S. P., is cholesterin in combination as esters of fatty acids. *Adeps lanæ hydrosus* with drugs makes stable emulsions which readily penetrate the skin and carry medicaments with them. Cholesterin is odorless, insoluble in water, but soluble in alcohol, which on evaporation leaves it in rhombic plates (Fig. 84).

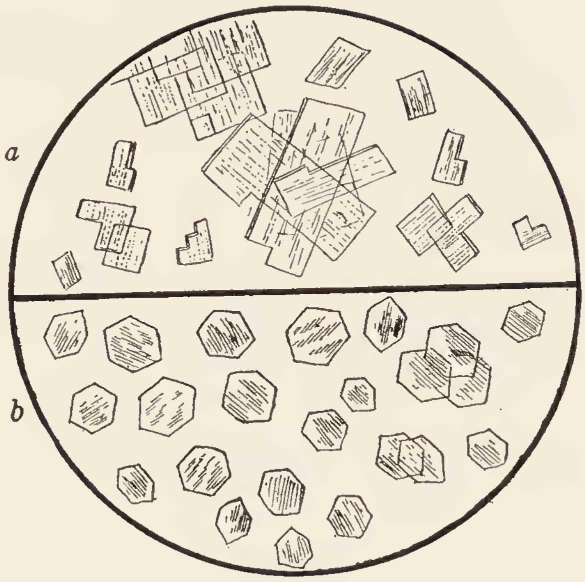


FIG. 84.—*a*, Cholesterin crystals; *b*, cystin crystals (Salinger and Kalteyer).

Gall-stones are sometimes small and easily passed, though the concretion, which in passing the bile-duct gives hepatic colic, is ordinarily the size of a small die. The concretion may be as large as the gall-bladder. It may be solitary, though they are usually multiple. For each flat facet on the surface, one other stone must have compressed it. They are usually polyhedral. The color varies in different stones—white, yellow, green, red, or black. When first voided they are soft and friable, or waxy and soapy. On keeping they become hard. The specific gravity varies from 0.8 to 1.15. A transverse section shows usually a nucleus of cholesterol crystals or pigment surrounded by a zone of radiating structure and a cortex that is in concentric layers. The average composition is 70 or 80 per cent. cholesterol with pigment, but it may be mainly pigment or calcium carbonate.

The **bile pigments** are chiefly two, bilirubin and biliverdin. They are formed by the breaking up of hemoglobin. The bile of carnivora is yellow because bilirubin predominates in it; that of herbivora is green from the abundance of biliverdin. The iron-free crystals of hematoidin found in old blood-clots are identical with bilirubin, and go to prove its derivation from hemoglobin (Plate 4, Fig. 2). Bilirubin, $C_{16}H_{14}N_2O_3$, when oxidized by the air or by nitric acid, takes up 1 atom of oxygen and becomes

biliverdin, $C_{16}H_{18}N_2O_4$. In Gmelin's test with nitric acid (p. 569) the color changes with the successive degrees of oxidation into green, blue, and red pigments, and finally to yellow *choletelin*, $C_{16}H_{18}N_2O_6$. By reduction processes in the intestine the bile-pigments yield *hydrobilirubin* or *stercobilin*, the pigment of the feces. A portion of it is absorbed and finally escapes from the body as the pigment *urobilin* of the urine.

The **rôle of bile** is to a great extent that of an *excretion* of cholesterin, metallic salts, lecithin, and altered blood-pigments. It does not contain enzyms, but acts as an auxiliary to the pancreatic juice, neutralizing the acid gastric juice from the stomach, assisting in the saponification and absorption of fat and the digestion of starch. As some of its constituents are absorbed by the intestine for further use it may also be regarded as a *secretion*.

INTESTINAL JUICE

In addition to the pancreatic juice and bile the mixed secretions of the duodenal (Brunner's) and intestinal (Lieberkühn's) glands have a digestive action on the food after it leaves the stomach. This *succus entericus* appears to have no independent effect on native proteins or fats, though it probably has three ferments with the power of "inverting," severally, maltose, cane-sugar, and lactose. Together these are called *invertin* or *invertase*, because their effect on the dextrorotatory disaccharids is to hydrolyze and split them into dextrose and levulose, the latter inverting the direction of rotation of the polarized ray (p. 438).

The trypsinogen of the pancreatic juice has no proteolytic action until the trypsin is set free by an enzym of the intestinal juice called *enterokinase*.

Recent researches appear to demonstrate that the proteoses and peptones are not absorbed as such, but are probably first broken up to amino-acids and hexon bases in the intestinal wall by another ferment called *erepsin*, and that the various tissue substances are formed synthetically from these comparatively simple crystalline end-products. The protein molecule may be compared to a barrel made of staves of amino-acids. Digestion removes what may be called the hoops, and the staves fall apart. The synthetic powers of the tissue cells put them together again in such arrangements as are fitted to the structure of the tissue.

Experiment 1 (on Ox-bile).—Having observed its green color, bitter taste, odor, and alkaline reaction, take the specific gravity. It will be between 1020 and 1030.

Experiment 2.—Put a small quantity in a test-tube and add acetic acid. A string-white precipitate forms of mucin and nucleo-albumin.

Experiment 3 (*Pettenkofer's Test for Bile Salts*).—Shake together, in a test-tube, bile and a grain of cane-sugar. Pour strong sulphuric acid down the side; it makes a purple color in the fluid and froth. This denotes the presence of the biliary salts.

Experiment 4 (*Gmelin's Test for Bile-pigment*).—On a white plate or capsule smear a layer of bile and let fall upon it a drop of yellow nitric acid. A play of colors at the line of junction shows the stages of oxidation of bilirubin.

Krokiewicz's Test for Bile-pigment.—Take 5 drops each of a 1 per cent. aqueous solution of sulphanilic acid and a 1 per cent. sodium nitrite solution. Mix in a test-tube with an equal bulk of the liquid to be examined. If bile-pigment be present the mixture becomes ruby-red, which, on the addition of a few drops of HCl and dilution with distilled water, changes to an amethyst-violet. (With acid gastric juice the addition of HCl is usually unnecessary.)

Experiment 5.—*Cholesterol* in a concretion supposed to be biliary or in a piece of lanolin may be shown by dissolving a portion of the concretion in warm alcohol and evaporating a few drops on the slide of a microscope. Rhombic plates form (Fig. 84), and if heated with a drop of strong sulphuric acid, they turn red at the edges.

Salkowski's Test.—Having dissolved cholesterin in chloroform, gently shake with an equal quantity of strong sulphuric acid. A blood-red color appears in the solution, while the acid takes a green fluorescence. Poured on a white plate, the chloroform gives a play of colors, blue, green, and yellow.

BLOOD

The composition of the blood varies according to the part of the system from which it is taken, and according to the conditions of food and fasting, exercise and rest, health and disease. It is always a red or purple, neutral reacting liquid, with a characteristic odor. While circulating in the body, it is shown by the microscope to consist of a fluid, *plasma*, carrying in suspension minute bodies, the red and white *corpuscles* and the platelets. These corpuscles constitute 40 per cent. of the volume of the blood and 48 per cent. of its weight, and the red ones are sufficient in amount to give to the blood its crimson hue (Fig. 85) (p. 536).

In freshly drawn blood the *red* corpuscles are characterized by their color, their biconcave shape, and their tendency to form

columns like rolls of coin. They consist of a membrane and semi-fluid contents, which change under reagents into a colorless elastic stroma and a red coloring-matter. The *white* corpuscles are found in the spaces between the rolls of red corpuscles. They are grayish and globular. They consist of a transparent substance

FIG. 85.—Cells of blood: *a*, Colored blood-corpuscles seen on the flat; *b*, on edge; *c*, in rouleaux; *d*, blood-platelets (Leroy).

embedding granules—fatty, proteid, and carbohydrate. They have nuclei and are capable of ameboid movements. They can protrude and retract portions of their bodies, and thus envelop and expel foreign bodies. They can also squeeze through the walls of the capillaries. By staining they can be differentiated into four forms, believed to be stages in development (Fig. 86), *small*, *large*,

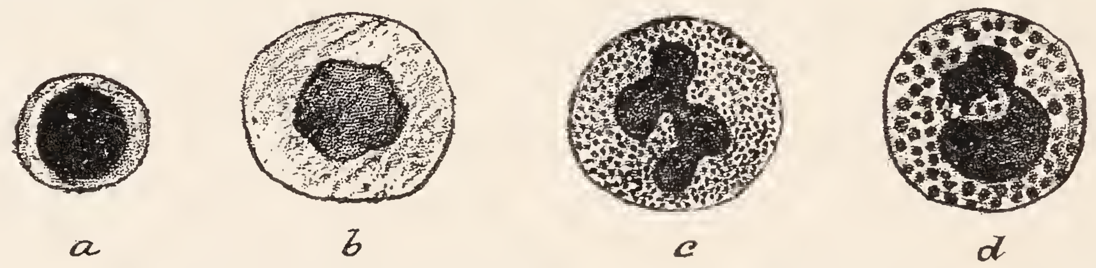


FIG. 86.—Various forms of leukocytes: *a*, Small lymphocyte; *b*, large lymphocyte; *c*, polymorphonuclear neutrophile; *d*, eosinophile (Leroy).

mononuclear, *polymorphonuclear*, and *eosinophile* or "over-ripe" cells. The *blood-platelets* are distinct normal cells, grayish white and without nuclei. They appear to be involved with the corpuscles in aiding coagulation.

The red corpuscles are produced chiefly in the marrow of the long bones; the white are derived from the lymphocytes of the lymph-glands. The red corpuscles are carriers of oxygen; the white are the *phagocytes* or scavengers, destroying and removing particles of disintegrated tissue and the invading bacteria of disease.

The blood coloring-matter is treated of in another place (p. 536).

Blood-plasma is the colorless liquid which bears food to the tissues and in which the cellular elements float. In its 8.9 per cent.

of solids the proteins constitute 6.9 per cent. and the inorganic salts 0.84, the remainder being carbohydrates, fats, and waste organic material. Sodium carbonate and disodium phosphate both contribute to give it an alkaline reaction. A proportion of phosphoric acid exists in combination with proteins. The protein substances are serum-albumin, serum-globulin (paraglobulin), and fibrinogen (metaglobulin). Varying amounts of oxygen and carbon dioxid distinguish arterial and venous blood. Oxygen to the extent of 0.26 per cent. is dissolved in the plasma; a larger amount, 22 per cent., circulates loosely, combined with the hemoglobin of the red corpuscles. Carbon dioxid to the extent of 40 per cent. exists in the plasma, partly as alkaline carbonates and partly as a loose organic compound. In the act of breathing air comes to the walls of the alveolar capillaries. At the body temperature there is a high rate of diffusion between the gases of the alveoli and those in the blood. Oxygen constantly passes into the blood and carbon dioxid passes out.

Coagulation.—While in the circulation, blood is a fluid of a specific gravity of about 1060. Soon after it is drawn from the vessels it suddenly becomes a solid jelly with a slight evolution of heat. On standing, the clot contracts, leaving a straw-colored liquid called *serum*. The clot itself is composed of corpuscles enclosed in a mesh of *fibrin*. Washing at the tap removes the corpuscles and leaves the shreds of fibrin. Coagulation is due to a change in the dissolved fibrinogen (metaglobulin), brought about by the presence of calcium salts and an enzym—*thrombase*. Calcium is necessary for clotting. The ferment appears to cause a combination of the fibrinogen with the calcium, resulting in the coagulated protein. Howell's theory of coagulation is that "In the circulating blood we find as constant constituents *fibrinogen*, *prothrombin*, *calcium salts*, and *antithrombin*. The last-named substance holds the prothrombin in combination and thus prevents its conversion or activation to thrombin. When the blood is shed, the disintegration of the corpuscles (platelets) furnishes material (thromboplastin) which combines with the antithrombin and liberates the prothrombin; the latter is then activated by the calcium and acts on the fibrinogen. According to this view the actual process of coagulation involves only three factors: fibrinogen, prothrombin, and calcium. These three factors exist normally in the circulating blood, but are prevented from reacting by the presence of antithrombin." As the fibrin comes out of the plasma, there is left the *serum*. This retains two proteins—albumin and globulin—and the enzym—thrombase. If magnesium sulphate be added to saturation, the globulin is precipitated. After filtration the filtrate contains albumin, which is precipitated by saturation with ammonium sulphate. After filtration

of this precipitate the filtrate does not respond to tests for proteins—*i. e.*, nitric acid, heat, and the biuret reaction.

Biologic Test.—In another place (pp. 529 and 530) definitions have been given of the terms hemolysin and precipitin. When an albuminous substance from one animal is injected into another of different species, "antibodies" form, which precipitate it. This *precipitin* is specific for that albumin and distinguishes it from all others, even when by ordinary chemical or physical reactions no difference can be detected. After cows' milk has been injected into the peritoneum of a rabbit the serum of the rabbit precipitates the casein of cows' milk, but has no effect on the milk of other animals. When a rabbit has been immunized by repeated injections of small quantities of human blood, peculiar hemolysins and precipitins are found in the blood-serum of the rabbit. This serum has a hemolysin which disintegrates human blood-corpuscles and precipitates dilute human serum when in the proportion of 1 : 100, but not that of the ape until the concentration is 1 : 30, nor that of the dog until it reaches 1 : 10. It appears that though the precipitin is specific, the blood of other animals may show some proportions of it, according to the closeness of their relationship. By means of this test blood-stains can be traced to their origin in man or in some species near him in the animal scale. For this purpose the stain is dissolved in 0.9 per cent. salt solution and filtered.

Experiment 1.—Defibrinated blood may be obtained at the slaughter-house by whipping freshly drawn blood with a bundle of twigs. The fibrin collects on the twigs and the remaining blood keeps fluid. Test the reaction with neutral litmus paper. After washing away the blood a blue stain shows alkalinity.

Experiment 2.—Put in a test-tube 5 c.c. of hydrogen peroxid, add a few drops of blood, and note the foam caused by oxygen bubbles escaping from the peroxid. The blood is a catalytic agent, from the presence of *catalase*, and also from a *peroxidase* (p. 546).

Experiment 3.—*Guaiac Test.*—Put a small lump of freshly broken gum guaiac into a test-tube containing alcohol and boil until deep yellow. Filter and add filtrate to dilute blood to make an emulsion. Pour in gently hydrogen peroxid; a blue ring forms. If the quantity of blood is small, then a few drops of the emulsion is added to a fragment of sodium perborate on a white plate. The fragment turns blue and changes later to green. (p. 639).

Experiment 4.—Having dried a drop of blood on the slide of a microscope, add glacial acetic acid, cover, and warm until bubbles appear. On examination Teichmann's *hemin* crystals are seen (Plate 4, Fig. 3).

Experiment 5.—With a spectroscope note the changes in the absorption bands induced by deoxidation of diluted blood with ammonium sulphid and gentle heat. Observe the return of bands after pouring the blood back and forth several times to get oxygen from the air. Saturate with coal-gas and note that the bands now are not changed by ammonium sulphid, as the carbon monoxid hemoglobin is a fixed compound not susceptible to reduction and oxidation (Plate 4, Fig. 1, e).

FECES

Normal Feces.—The absorbents of the intestines take up the diffusible principles of the food mass. The undigested remainder is passed on by peristaltic action and is joined by excretory products to be extruded in defection. Even when the feces are consistent the most abundant constituent is *water*, about 75 per cent. While the moist total weighs about 100 gm. or 3 troy ounces, the *solid* residue of dry feces on a mixed diet averages about 25 gm. or 6.5 drams.

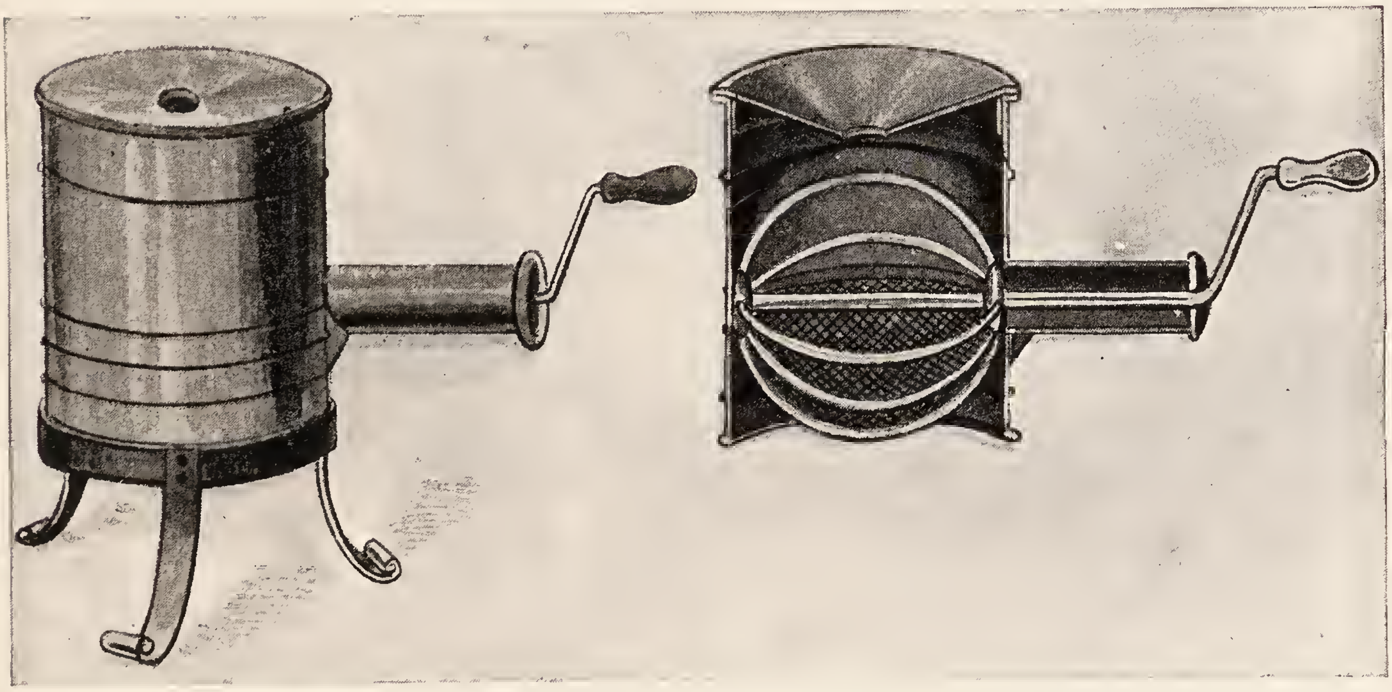


FIG. 87.—Einhorn's stool sieve (Kemp).

A small proportion is nutritious food that has escaped absorption. A larger percentage is made up of the constituents which are digestible with difficulty, such as uncooked starch, tendinous and elastic tissue, and certain salts of the alkaline earths. Still larger is the amount of indigestible matter, such as cellulose, mucin, keratin, resins, gums, chlorophyll, and cholesterin. In decomposing, the protein and fat yield unabsorbed by-products, such as indol, skatol, phenol, fatty acids, insoluble soaps of calcium and magnesium, lactic acid, and hematin. Always much organized material is found, such as masses

of bacteria averaging 8 gm. or 2 drams, about one-third of the normal feces and epithelial débris, 4 gm. or 1 dram, one sixth of the total. Very characteristic are the bile-products, hydrobilirubin, bile acids, and cholesterin.

Clinical Examination.—Careful inspection by the eye and the microscope gives more diagnostic aid than the chemical tests. To determine the **naked-eye characters,** spread out the soft stool in a large dish. If too solid, the material may be washed on a fine meshed sieve, or placed in a flour-sifting apparatus, shown in Fig. 87, and the handle turned slowly under a running tap. This retains the coarser particles only. The significant objects may be gall-stones or *biliary calculi*, which are usually light, floating, rounded masses about

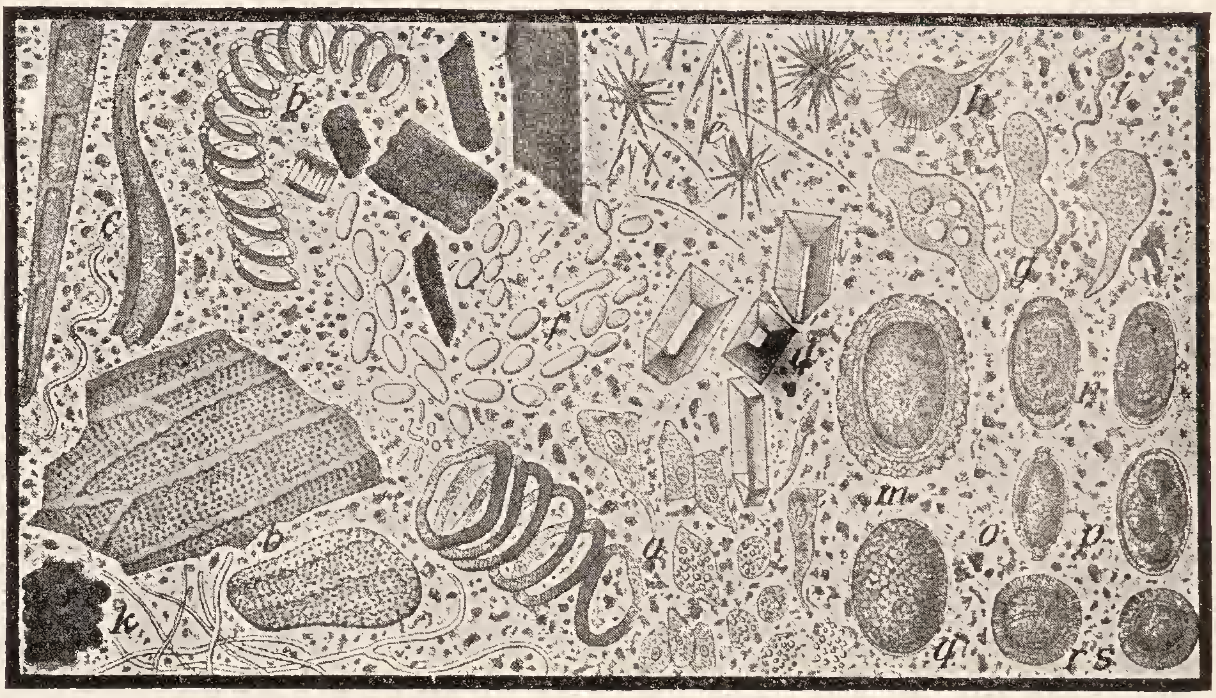


FIG. 88.—General view of the feces: *a*, Epithelial cells and leukocytes; *b*, stone-cells; *c*, cuticular formations; *d*, crystals of ammoniomagnesium phosphate; *e*, fat-crystals; *f*, yeast-fungi; *g*, Amœba coli; *h*, Trichomonas intestinalis; *i*, Cercomonas intestinalis; *m*, ovum of ascaris; *n*, ovum of oxyuris; *o*, ovum of trichocephalus; *p*, ovum of ankylostomum; *q*, ovum of bothriocephalus; *r*, ovum of Tænia saginata; *s*, ovum of Tænia solium (Jakob).

the size of a die, colored green or brown by bile and composed mainly of cholesterin (p. 567). Perhaps *pancreatic* concretions may be present. These contain no cholesterin or bile-pigment, but consist of calcium phosphate and carbonate. Hard lumps of dry feces are called *coproliths*. Concentric layers of hard insoluble soaps and earthy phosphates form *enteroliths*.

The **color** on a normal mixed diet is yellowish brown from hydrobilirubin. Owing to the excess of hematin a diet rich in meat yields very dark stools, whereas a milk diet free from coloring matter gives a pale result. With children the bright yellow bilirubin of bile is not reduced to hydrobilirubin as in adults. Occasionally, the normal bilirubin yellow changes by oxidation to green biliverdin. Blueberries impart a blackish hue and so do doses of iron and bismuth salts, forming black oxids and sulphids. When the bile-duct is ob-

structed, absence of bile causes a grayish-white color. A red or brown-black color may be due to blood.

Odor.—Normally, the odor is characteristic of skatol and indol derived from putrefaction of protein. On a meat diet this is very marked, less so on a vegetable régimen, and barely noticeable on a milk diet. Hydrogen sulphid and methyl mercaptan intensify the disagreeable quality.

Microscopic Characters.—Rubbed in a mortar with physiologic salt solution (p. 225) the solid stools yield a suspension of minute objects for microscopic study. The normal objects are to be seen in Fig. 88. The food residues are muscle-fibers, as yellow oblong, rounded bodies with barely visible striations; fibers of connective and elastic tissues; irregular starch grains which color blue by Gram's solution of iodin; fat globules which take a red stain from Sudan III; needles and crystals of fatty acids and soaps of magnesium and calcium; vegetable cells; leukocytes, epithelium, mucus, bacteria, crystals of cholesterin and of hematoidin. Among the parasites to be sought for under a low power are the eggs of various intestinal worms, or even the entire worm when small as is the hook-worm (Fig. 89).

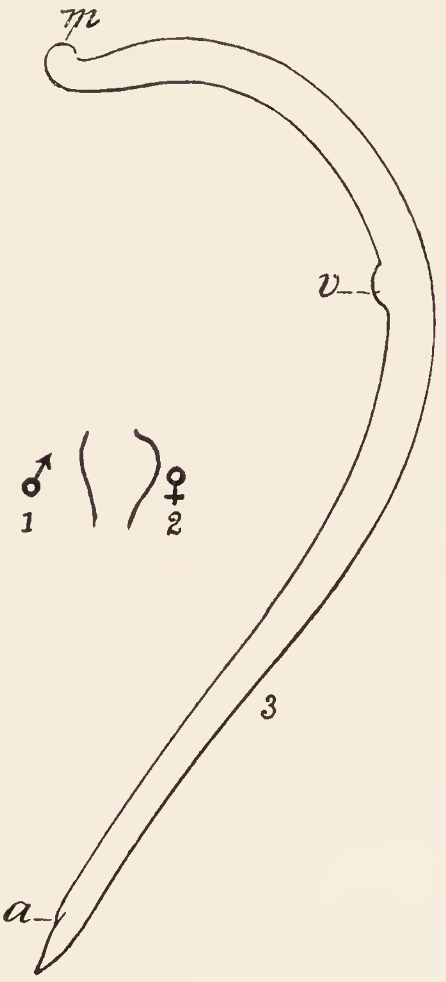


FIG. 89.—New World hook-worm (*Uncinaria Americana*); natural size: 1, Male; 2, female; 3, the same enlarged to show the position of the anus (*a*), the vulva (*v*), and the mouth (*m*) (after Stiles).

CHEMICAL TESTS

The Sample.—In order to determine the effect of digestion upon a prescribed meal, the resulting stool is definitely separated by administering a gelatine capsule, containing 3 gr. charcoal, at the beginning and the end of the observed period. In twenty-four hours the stools show two boundary zones of black as the result.

Reaction.—This is taken by spreading a small piece of moist, mixed feces upon a piece of litmus paper. The color change is seen on the reverse of the paper. Normally, the reaction is slightly alkaline or amphoteric, but occasionally it is neutral, or on a vegetable diet it may be acid. In the infant, acidity is the rule.

Fat and Cholesterin.—Merely to detect fat is of no value as it is constantly present in small amount, but a quantitative estimate may be of help in diagnosis. After drying and weighing a portion of the

stool, extract the fat with ether in the Soxhlet extractor (Fig. 96) and evaporate to dryness. This gives fat and cholesterin. The fat is saponified by adding for 1 gm. of fat $1\frac{1}{2}$ gm. of solid potassium hydroxid and 25 c.c. of alcohol and boiling on a water-bath for one-half hour, replenishing the alcohol to the same volume. To this mixture of soap and cholesterin add sodium chlorid powder and extract the cholesterin by shaking with ether. Separate the extract and on evaporation the dry residue will show microscopic crystals (Fig. 84) of cholesterin.

Clinical Import.—When the bile flow is stopped or diminished while the average proportion of fat in the food is maintained, the undigested fat may be visible to the naked eye, amounting sometimes to 50 per cent. of the stool. Pancreatic disorder is denoted by the appearance of fat, carbohydrates, and protein unabsorbed because undigested.

Blood.—Its presence is betrayed to the naked eye by the unchanged red color, when the hemorrhage is from the lower bowel. When the source is the upper intestine, the color is altered to brown or black, so that a test is necessary to distinguish it. For a small amount to be significant of hemorrhage, the possibility must be excluded that the hematin is derived from blood or meat in the food.

For the spectroscope or hemin tests a portion of the feces is shaken with water containing a little acetic acid, and the blood-pigment is separated from this suspension by shaking with ether. The ethereal extract is brown red and gives the characteristic band *h* (Plate 4, p. 537).

Occult Blood.—When the amount is so small or so evenly distributed that the color change in the stool is not visible, blood may still be detected by the benzidin and the guaiac tests. As these are liable to react with oxidizing enzyms, a small sample of the stool is prepared for testing by first agitating with water 5 c.c. and heating the suspension to boiling. The reagents are applied to this aqueous mixture by the methods given on pp. 572, 638.

Clinical Import.—As a rule, blood-cells are so altered by intestinal digestion that they are not found when hemorrhage is from above the sigmoid flexure. Ulcers of the mucosa, new growths, invagination, and stenosis all may cause hemorrhage, but the site of the lesion is discovered only through the other clinical signs.

Bile-pigments.—A small portion of the feces is shaken with a saturated aqueous solution of mercuric chlorid. After standing in a shallow dish for twenty-four hours any particles containing hydrobilirubin show a deep red color. A green color of biliverdin is imparted by their oxidation when the particles contain bilirubin. Confirmation is obtained by *Gmelin's test.* A drop or two of liquid feces added to a few drops of yellow nitric acid cause a play of colors if bilirubin be present (p. 568).

Clinical Import.—Absence of bile-pigment denotes biliary obstruction. Unchanged bilirubin and biliverdin are found in catarrhal states and too active peristalsis.

Bile Acids.—A small portion of the stool is extracted with alcohol filtered and the filtrate evaporatd to dryness. The residue is dissolved in water alkaline with sodium hydroxid and tested for bile acids with Pettenkofer's test (p. 569).

Clinical Import.—In health the bile acids are completely reabsorbed. Something is wrong if they escape with the feces, as in the dyspeptic diarrheas of children.

Carbohydrates.—The residue after extraction of fat from feces with ether is treated with water, boiled, filtered, and the filtrate evaporated to a small volume. With this sugar is determined by Fehling's method (p. 618). Starch is revealed by the iodin test (p. 146). To calculate the amount of starch, convert it all to glucose by prolonged heating with hydrochloric acid and titrate with Fehling's solution (p. 618).

Clinical Import.—Sugar is not present in feces normally, but may be left in it unabsorbed as a result of dyspeptic diarrhea. A small amount of starch may be contained normally, but with disorder of the pancreas more of it escapes absorption from failure of amylotic digestion.

Protein.—As the fecal nitrogen comes mostly from bacteria, epithelial débris, mucus, and other secretions, its determination throws no light upon the activity of proteolytic digestion.

EXAMINATION OF MILK

Properties.—Normal milk is a sweet, opaque, bluish-white fluid, with a peculiar odor, holding in solution caseinogen, albumin, sugar, and mineral salts. Its opacity is due partly to the minute butter globules which are suspended in it and partly to the caseinogen of difficult solubility.

Percentage composition of normal milk.	Cow.	Human.
Water	87.41	87.29
Solids, as tabulated below	12.59	12.71
Caseinogen	3.01	1.03
Albumin	0.75	1.26
Albuminoids	3.76	2.29
Butter or fat	3.66	3.78
Milk-sugar	4.92	6.04
Ash	0.70	0.31

Microscopically, the milk is composed of minute, brilliant *fat-globules* suspended in clear plasma. Immediately after birth of the child human milk is relatively poor in casein, but rich in fatty matter, which exists in the form of *colostrum* masses (Fig. 90). In this list of constituents are found representatives of all classes of foodstuffs: caseinogen and albumin of the proteins; emulsified fat (olein, palmitin, butyrin, and stearin); lactose of the carbohydrates. Among the inorganic food principles indicated by the ash are traces of calcium phosphate and other salts with citric acid. These are mixed in such proportions as to make a complete diet for the infant, and even for the adult when supplemented with such simple fare as green vegetables and bread or fruit. While it is possible to maintain the caloric needs of the adult body on milk exclusively, yet, as three or four quarts would be required, it is objectionable from the resulting discomfort of distention and excessive urinary flow. It is employed in the diet of fevers, of gastro-enteric derangements, in diseases of the liver, and in acute and chronic nephritis.

Morbid Milk.—Human milk is injured by excessive emotion or ill-health of the mother and by the administration to her of certain drugs that pass into the milk. Cows' milk is affected in the same way by diet and by disease, such as tuberculosis, foot-and-mouth disease.

Reaction.—Human milk turns red litmus paper blue, showing alkalinity. Cows' milk is usually alkaline or neutral when fresh, though sometimes acid when delivered in cities, and occasionally a sample will be found that is amphoteric—that is, reddens blue litmus paper, and turns red litmus paper blue. This is ascribed to the presence of the acid phosphates which dissociate hydrion with the secondary phosphates, which are alkaline from the hydroxidion they dissociate by hydrolysis (p. 188).

Quantity.—The average secreted daily by a woman is 1 L., or 2 pt.

Spontaneous Change.—If milk stand for several days in a warm place, it coagulates and *sours*—that is, turns acid by fermentation of the sugar (lactose) into lactic acid, $C_6H_{12}O_6 = 2(C_3H_6O_3)$. The coagulum consists of *casein*, which previously existed in a soluble form of union with calcium phosphate as caseinogen. This curd of casein can be produced by any acid, as in the following experiment:

Experiment 1.—**Acid Curd.**—To half a test-tubeful of diluted milk (1 : 3) add a drop or two of acetic acid, and gently warm; an abundant precipitate falls. This precipitate is the curdled casein, carrying with it most of the fat.

Experiment 2.—Put into a test-tube 1 c.c. of milk and 20 c.c. of water. Add a few drops of solution of copper sulphate and a few drops of potassium or sodium hydroxid to throw down the proteins

and fat. When the precipitate falls, decant or filter off the clear liquid. Boil this with Fehling's solution: a red or yellow precipitate means sugar (lactose).

Experiment 3.—**Proteins.**—Mix equal volumes of milk and Millon's reagent in a test-tube and boil. A red precipitate proves the presence of proteins (casein and albumin).

Milk-sugar and Salts.—Having filtered the whey from the acid curd and tested the filtrate with Fehling's solution, it is seen that the milk-sugar reduces the cupric salt and precipitates the yellow or red oxid. If to another portion we add magnesia mixture, the phosphates are precipitated. On adding to another portion silver nitrate, the chlorids are precipitated, insoluble in nitric acid.

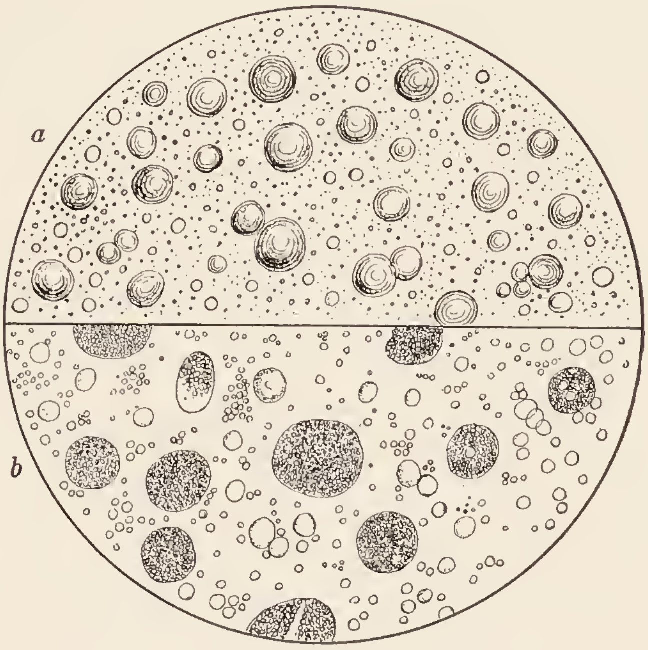


FIG. 90.—*a*, Milk; *b*, colostrum (Wolf).

Butter.—In cows' milk ether will not dissolve the fat-globules unless they are liberated by removing their envelopes with acetic acid, caustic potash, or soda. With human milk it suffices to agitate vigorously with ether alone. In churning, the envelopes of casein are ruptured mechanically, and the fat-globules cohere in large masses of butter. This process does not separate all the fat as butter. The residue, called *buttermilk*, still contains about 1 per cent. of fat. As it is formed from ripened cream, buttermilk contains lactic acid formed at the expense of the lactose. We may separate the fat by the following experiment:

Experiment.—To a test-tube one-third full of milk add half its volume of potassium hydroxid and half of ether; shake the mixture and stand in a warm place. The milk clears up, and the butter dissolved in the ether floats at the top. By separating the ethereal layer and evaporating it, a residue of butter is left.

Pepsin Curd.—The first act in the digestion of milk is the conversion of caseinogen to casein, and its coagulation by the rennin of the gastric juice. This can be shown artificially by the following experiment:

Experiment.—Into a test-tube about one-third full of milk put a few drops of neutral essence of pepsin (Fairchild's). Mix gently, warm to the temperature of the body, and keep at 40° C. (104° F.). A solid *curd*, containing fat entangled by the casein, forms in ten or twelve minutes, so that the tube can be inverted without losing

the milk. In a short time a *whey* separates from the clot. If the experiment be performed on human milk, the coagulum is not a lump of curd, but floating flocculi. If cows' milk be boiled or if it be largely diluted with lime-water, the same loose flocculi form when it is curdled with pepsin.

Experiment.—Add a few drops of dilute hydrochloric acid to the pepsin curd, so as to make with the pepsin an artificial gastric juice, and set aside at 40° C. (104° F.) for two or three hours. The curd is digested and gradually dissolves to make a yellowish fluid with the peculiar odor and bitter taste of *peptonized milk.*

If the milk be previously boiled, or if the rennet be boiled, the ferment will not work.

In the creameries the curds are a by-product from which alkali or sodium combinations with casein are produced and used as condensed foods under the names "plasmon" and "nutrose."

Methods of Preservation.—To prevent the lactic-acid and other fermentations, several procedures are resorted to, such as refrigeration, sterilization, pasteurization, and the addition of preservatives.

Refrigeration.—If a sample of fresh milk, tested with litmus paper, be put in a refrigerator kept at or below 10° C. (50° F.) for several days, the reaction will be but little changed, the milk having kept sweet and uncurdled. Cold will not preserve milk indefinitely, nor will it kill bacteria, nor alter toxalbumins after they have been formed.

Sterilization.—Fresh milk boiled for twenty minutes forms a scum, due to dissociation of casein compounds as the result of drying at the surface. If skimmed off, the pellicle forms again when boiled. By excluding the floating dust of the air with a plug of cotton, it will keep sweet and uncurdled for several days, owing to the death of the bacteria which cause lactic fermentation. So far as infection is concerned, milk sterilized by boiling is perfectly safe; at the same time it becomes less palatable and the casein and albumin are altered probably by the fixing of calcium salts, precipitation of lactalbumin, of calcium and magnesium phosphate, and of citric acid as tricalcic citrate. Boiled cows' milk does not form such large and tough curds in the stomach as does the raw milk, and hence in many cases is more digestible. On the whole, such small differences as are found in nutritive value between raw and boiled milk are in favor of the latter. If in a given case there be any doubt on this head, it must be remembered that lower degree of heat will suffice to prevent the growth of bacteria for a short while and yet not injure the milk in taste or as an assimilable food.

Normally, it contains several enzyms in small amount, *galactase* which digests proteins, *amylase* for carbohydrates, and *lipase* for

fats. These favor the digestion of milk, but are rendered inactive by heat above 75° C. (167° F.). Below this point[1] it does not lose the taste of fresh milk nor become less digestible. At this temperature and as low as 65° C. (150° F.) the matured disease germs are killed, and the spores so much weakened in vitality that all liability to cause intestinal disorder is removed if the milk be used within twenty-four hours of the treatment.

The *flash* process heats milk momentarily to 85° C. (185° F.). This damages the milk as a food in taste and is not so effective in sterilizing as the *holding* process at a lower temperature. This is performed by holding it at 63° C. (145° F.) for thirty minutes. It suffers no appreciable chemical change and is free from bacterial danger.

Pasteurization.—Having put some fresh milk in a clean boiled glass bottle, stoppered with a plug of cotton, stand it in a vessel in which the water-level is as high as the level of the milk. Heat until the thermometer suspended in the water reaches 63° C. (145° F). Remove vessel and contents and cover with a blanket for thirty minutes. The bottle of milk is then taken out, cooled quickly in running water, and kept in a cold place. It will keep sweet much longer than milk not pasteurized.

Freeman's Pasteurizer.—A simple apparatus which any nurse can use with accurate results is the pasteurizer devised by Freeman. It consists of a metal pail, into which fits a receptable holding the bottles. The receptacle is so made that each bottle fits into a separate small metal cylinder. The pail is filled with water to the level of the groove running around it, placed on the stove without the milk receptacle, and the cover put on. While waiting for the water to boil the proper amount of milk for each feeding is put into each bottle, the bottles plugged with raw cotton, and placed in the receptacle. Water is then poured around them into each cylinder, in order to prevent the direct action of the hot water in the pail from cracking the bottles. As soon as the water in the pail is boiling, the pail is removed from the fire and placed out of the draught upon a non-conducting substance. The lid is now removed, the receptacle put in, and the lid reapplied. It is left thus for forty-five minutes, when the lid is removed and the receptacle elevated so that it rests upon supports which hold it partially out of the pail, and a stream of cold water is now turned into the pail for fifteen minutes. The bottles are then kept on ice till needed. The principle of the apparatus is the fact that the given quantity of water which is in the pail will,

[1] A constant constituent of unheated milk is an *oxidizing* enzym. Its absence may be regarded as proof that the milk has been heated for preservation. The *test* for it is to mix with 10 c.c. of milk 1 c.c. of fresh tincture guaiac, 5 c.c. of turpentine, and 5 c.c. of hydrogen dioxid. Unheated milk gives a blue color.

in cooling, elevate the temperature of the milk to the desired degree, so that the two liquids become of the same temperature at 68° to 69° C. (154°–156° F.). Receptacles are made either for 10 six-ounce bottles or 7 eight-ounce bottles, and either receptacle will fit into the pail.

In the absence of a thermometer or special apparatus, resort may be had to the following rough method: A basin containing several inches of water is placed on a slow fire and the cotton-stoppered bottles of milk placed in it. After boiling the water for ten minutes the milk, which has not boiled, but only simmered, is removed and kept in a cool place until used.

If the milk be not tolerably fresh, poisons may have developed already. Pasteurizing will not destroy the toxalbumins or dissolved poisons when once produced, nor render stale milk harmless.

Test for Pasteurized or Sterilized Milk.—Heat two samples of milk, one, *A*, to 70° C. (160° F.), the other, *B*, to 80° C. (176° F.). When cold, test both separately by adding to each a small amount of solution of paraphenylendiamin ($C_6H_4(NH_2)_2$), and then a few drops of hydrogen dioxid. The unchanged enzyms in *A* cause instantly a deep-blue color; the overheated *B* does not turn blue for some time.

Preserved Milk.—By evaporation of skimmed milk in a vacuum and adding sugar, a soft solid is obtained, which is used by travelers as a substitute for fresh milk. It is sealed in tin cans and sold as *condensed* milk. It is mixed with coffee, or it may be taken as a beverage in 1 : 10 dilution with water. To prevent bacterial changes in fresh milk it is quite common to add formaldehyd or boric acid, either of which is tasteless in the amounts used.

Formaldehyd is usually added as formalin, under the trade names of *Preservalin* and *Freezene*, in the proportion of 1 : 40,000, less than 5 drops in a gallon. While it certainly enables milk to be kept longer in warm weather, there is some evidence to the effect that it retards slightly the digestion of protein material, although without any injurious general effect.

Boric acid and borax are employed as preservatives by adding to 1 qt. of milk 10 gr. of mixture of equal parts of borax and boric acid, or 35 gr. of boric acid to the gallon.

It is not likely that this amount would cause injury to the average healthy adult, taking an ordinary quantity of milk with other food, but it would very likely lessen the digestibility if not prove hurtful in the case of invalids and infants (p. 209).

Salicylic acid in milk may be detected by precipitating fat and proteins with mercuric nitrate and acetic acid, filtering and agitating the filtrate with ether, which dissolves the salicylic acid. After separation, the ethereal solution is evaporated and yields the

acid in crystals. These are dissolved in alcohol and tested by ferric chlorid, which gives a violet color; or else they are heated with a mixture of methyl alcohol and sulphuric acid, when the odor of wintergreen reveals the presence of salicylic acid.

In a similar manner *benzoic acid* is separated and identified by its reaction with ferric chlorid or cupric sulphate.

Detection of Formaldehyd in Milk.—Boil the suspected sample, 1 part, with 4 parts of commercial or yellow hydrochloric acid, which contains a trace of a solution of ferric chlorid. If no purple color result on cooling, dilute with an equal part of water, add a trace of ferric chlorid, and boil again. The purple reaction will sometimes appear better in the weaker solution.

Hehner's Test.—The same reaction follows the test made by mixing 1 c.c. each of milk and water, and pouring the mixture gently on 4 c.c. of strong commercial sulphuric acid which has a trace of ferric sulphate or chlorid. If the sulphuric acid is pure, add a drop of solution of ferric chlorid. The line of contact is blue or purple when formaldehyd is present, but with pure milk it is green. This reaction is due to the protein of the milk in the presence of a minute quantity of formaldehyd. It will detect 1 part of the latter in 250,000, and shows better when the proportion of protein is large. Hence if the purple does not appear at first, dilute the milk with thinned milk of known purity, and try again.

Rimini's Test.—See p. 650.

Detection of Boric Acid or Borax by the Turmeric Test.—Place in a porcelain dish 1 drop of the milk with 2 drops of strong hydrochloric acid and 2 drops of a saturated turmeric tincture. Dry the mixture on a water-bath; cool, and add a drop of ammonia by a glass rod. A slaty-blue color, changing to green, indicates borax. A drop of milk containing $\frac{1}{1000}$ gr. of borax will give this reaction.

Specific Gravity.—The hydrometer employed for taking the specific gravity should be very accurate and carry a scale for the usual variations of milk, or between 1000 and 1040. The *lactometer* of the New York Health Board is a hydrometer with a scale on which 100° stands for a specific gravity of 1029 (the minimum density of pure milk), while 0° stands for the specific gravity of water, and 120° for 1034, the maximum range of pure milk. On this instrument 1° is read as 1 per cent. of milk in the sample.

For cows' milk care should be taken to shake cream and milk together before testing.

To suit the small amount with human milk smaller instruments are used.

The sample taken for examination should be from the middle of the nursing or when the breast has been about one-half emptied, as the first milk is always poorer and the last richer than the average.

The specific gravity should be taken at a temperature of from 18° to 23° C. (65°–72° F.). By giving the stem of the lactometer a twirl as it is introduced, it readily settles to the proper level, which may otherwise be prevented by the adhesion of the milk to the glass, especially in a rich specimen.

The specific gravity of dairy milk, the product of a number of cows, should never fall below 1029. When lower than this, it is usually due to adulteration with water; but very rarely the low density is due to excess of cream in very rich milk.

The **quantity of cream** is measured by an instrument known as a *creamometer*, or a 10 c.c. glass-cylinder graduate may be used. Having mixed the milk thoroughly, a sample is poured into the vessel up to the highest mark. After twenty-four hours, at a temperature between 15° to 24° C. (60°–75° F.), the depth of cream layer thrown up is read, each degree of the scale being 1 per cent. The average sample of cows' milk would be 12 per cent. If the cream form 20 per cent. of the column, the sample would probably also show a low specific gravity. The accuracy of this test is affected by the length of time since milking, by the amount of previous agitation of the milk, by the fact that dilution causes a more rapid separation of the cream, by the temperature, and other variable conditions. It may serve a useful purpose when taken in consideration with other observations. In sorting cows' milk it may be assumed that:

Less than 10 *per cent. of cream in a milk of specific gravity above* 1033 *denotes skimming.*

Less than 20 *per cent. of cream, if joined to a specific gravity less than* 1020 *indicates watering.*

Clinical testing of mothers' milk is usually confined to taking the specific gravity with a small special lactometer and the percentage of cream in a small 10 c.c. graduate.

Human Milk

	Specific gravity, 70° F.	Cream—24 hours.	Proteins.
Normal average	1.031	7%	1.5%.
Healthy variations	1.028–1.029	9%–12%	Normal (rich milk).
" "	1.032–1.033	5%– 6%	" (fair milk).
Unhealthy "	Below 1.028	High (above 10%)	" or slightly below.
" "	" 1.028	Normal (5%–10%)	Low.
" "	" 1.028	Low (below 5%)	Very low (very poor milk).
" "	Above 1.033	High	Very high (very rich milk).
" "	" 1.033	Normal	High.
" "	" 1.033	Low	Normal (or nearly so).

Human milk presenting only moderate variations from the average—*e. g.*, specific gravity 1.028, cream 4 per cent., or specific gravity 1.033, cream 10 per cent., can usually be modified by appropriate treatment. If, however, the specific gravity is from 1.018 to 1.024, and the cream only 2 per cent. to 3 per cent., it is hopeless (Holt).

The **lactoscope of Feser** gives good results for ordinary testing of milk to determine its richness. The opacity of milk is due to the fat-globules, and is proportionate to the number of them. By measuring this opacity an approximate estimate can be made of the percentage of fat. For making this estimate roughly the *lactoscope* is very convenient. In the axis of a cylindric clear glass vessel (Fig. 91) and at its lower part (A) is a smaller cylinder of white glass, marked with a few black lines. In testing with this instrument, 4 c.c. of milk are introduced with the graduated pipet; the black lines are entirely concealed. Pure water is gradually added, while shaking, until the milk clears up sufficiently to make the black lines distinctly visible. There is a range of 1 per cent. between the point where the lines are first seen and that where they become sharply defined. By the graduation on the vessel the surface level of diluted milk can be read as percentage of fat in the original sample. The microscope having determined the absence of chalk, starch, or other suspended adulterants, a sample showing 3 per cent. and over is judged pure. Some rich Jersey milk shows 6 per cent. Any one experienced in its use will be accurate to within $\frac{1}{4}$ of 1 per cent. The main point is to see the lines well defined and not hazy. Having obtained the specific gravity by the lactometer, and the percentage of fat by the lactoscope, experiment shows that the proportion of total *solids* can be calculated by the formula of Hehner and Richmond.[1]

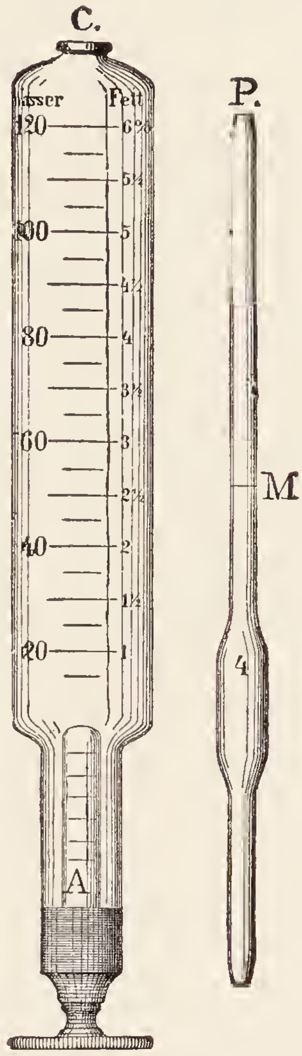


Fig. 91.—Feser's lactoscope.

A much simpler and less accurate method was devised by Heeren, whose *pioscope* consists of two disks. One of them is made of hard black rubber, in the center of which is a shallow, flat cell, of 22 mm. diameter, surrounded by a ring of 0.5 mm. in height, intended for the reception of a few drops of the well-mixed milk. The other disk is made of glass, colorless in the

[1] $$T = \frac{F + 0.2186\ G}{0.859},$$

in which F stands for percentage of fat, T, the percentage of total solids, and G, the specific gravity expressed in the last two units and any decimal ; thus, if the specific gravity is 1028.5, then G stands for 28.5. For example, if a specimen of milk had a specific gravity of 1030, and the percentage of fat was 4, then—

$$\text{Total solids} = \frac{4 + (0.2186 \times 30)}{0.859} = 12.3 \text{ per cent.}$$

center as far as is necessary to cover the central cell of the rubber disk, while on the margin are represented, in six sections, the various tints of cream, and milk from very rich to very poor. A comparison of the color of the milk in the central cell with the marginal color standards is rapidly made and gives results sufficiently approximate for the preliminary testing.

If a specimen of milk fail to satisfy the requirements of these physical tests, or if it become desirable to investigate more thoroughly for any other reason, the more exact methods of examination in the laboratory must be resorted to.

The **creamometer of Chevelier** (Fig. 92), or one of its modifications, may be used for this purpose. In this instrument the milk is left at rest for twenty-four hours to give time for the cream to rise, whose volume is then measured and readily shows whether the milk has been tampered with. After measuring and removing the cream the specific gravity of the residue may be taken, and shows by its lack of proper density the addition of water. In its simplest form the creamometer is a glass cylinder of about 35 mm. diameter and 170 mm. height. Measuring from below, marks are made, running around the cylinder at 50 c.c., 100 c.c., and 150 c.c. The interval between 100 and 150 is divided into 30 equal parts by short lines of division, and this graduation is extended to 10 of these units above 150 and below 100. Thus, the upper half is divided into 50 equal parts. Milk is poured into the instrument up to the uppermost mark of graduation, which also runs around the cylinder. After leaving it at rest for twenty-four hours the supernatant cream is measured, each unit of the graduation corresponding to 1 per cent. by volume. Good milk should not yield less than 10 per cent. of cream. After removal of the cream, the specific gravity of the residue is increased by 0.020 to 0.035 of the specific gravity of the fresh specimen before separation of the cream. A less voluminous layer of cream than ten subdivisions indicates that cream has been abstracted, and a smaller increase of the specific gravity indicates the additional dilution with water. The means of applying this test are simple enough, and it fairly approximates the true condition, but requires too much time to commend itself as a preliminary examination to be left to the subordinate inspectors. To reach close approximations with simple apparatus in a brief space of time, the optical behavior of milk is examined by Feser's lactoscope.

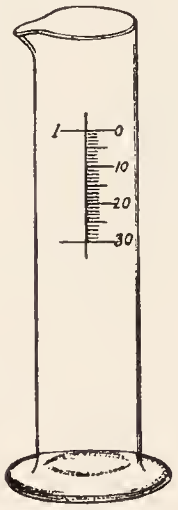


Fig 92.—Creamometer.

Modified milk is cows' milk altered by dilutions and additions in such a way as to bring its composition nearer to that of

human milk. The difference in the proportion of the two proteins, caseinogen and albumin, causes cows' milk to be less digestible in the human stomach. The gastric juice makes with human milk a slight flocculent curd, easily dissolved in the digestive juices. This is due to the small amount of caseinogen, which is the only protein coagulated by rennin. As cows' milk contains four times as much caseinogen and one-half as much albumin, it forms a tough, abundant curd of difficult solubility.

It is not possible artificially to produce the right proportion of the two proteins, but we can lower the proportion of caseinogen by dilution with water. Human milk averages about 2 per cent. more in sugar. Other differences, such as the alkaline reaction, will be noted on referring to the Tables of Composition at the beginning of this chapter. In the *milk laboratories* cows' milk is modified to resemble human milk by mixing milk, cream, lime-water, water, and milk-sugar in the right proportion for the age of the child. The exact formula varies according to the period of lactation, but an average human milk is closely imitated by a mixture of milk, 2 fl. oz.; cream, 3 fl. oz.; water, 10 fl. oz.; lime-water, 1 fl. oz.; and milk-sugar, 4 dr. It is customary to pasteurize the mixture and deliver it fresh in bottles stoppered with plugs of cotton to exclude bacteria.

When it is not convenient to have the milk mixture made at city laboratories, the mother will find useful a special glass graduate, called "*Materna*," which holds from 16 to 24 fl. oz. The outer surface is divided into seven vertical panels, and each of these is marked to show how much milk-sugar, milk, cream, lime-water, and water shall be mixed to get a product of a certain desired percentage strength for an infant of a certain age. The panels also show the percentages of fat, protein, and sugar in the measured amounts of the ingredients. The first is marked "fat 2 per cent., protein 0.6 per cent., sugar 6 per cent.," making a formula to be used at the beginning of an early weaning. The second panel is marked "fat 2.5 per cent., protein 0.8 per cent., sugar 6 per cent.," and the other panels show progressively increasing strengths.

Citrated Milk.—By adding 30 gr. of sodium citrate to 1 qt. of raw milk there is precipitation of calcium salts as citrate, so that dense clots are not formed by rennin and the milk is more digestible by feeble stomachs.

Milk Standards.—By the United States Treasury Department, cows' milk should contain by weight not less than 13 per cent. of solids and not less than 3.5 per cent. of fat. In Philadelphia it must have not less than 12 per cent. of solids nor less than 3.5 per cent. of fat. By the State of Pennsylvania it is required

to contain not less than 12.5 per cent. of solids and not less than 3 per cent. of fat. In the States of New York and New Jersey it should contain not less than 12 per cent. of solids, nor less than 3 per cent. of fat. The English Society of Public Analysts has fixed the standard for Great Britain as follows: Total solids, 11.5, fat, 3; solids not fat, 8.5 per cent.

Total Solids by Weighing.—The determination of total solids gravimetrically consumes considerable time, but it gives accurate results. Into a tared dish of platinum or a watch-glass 5 gm. of milk are weighed or 5 c.c. measured. The dish is then exposed to the heat of a water-bath for three hours. As evaporation is nearly done, it is now put into a water oven, and at intervals weighed until it ceases to lose weight. This constant weight, less the weight of the capsule, gives the *total solids*. The difference between the 5 gm. and the constant weight of the dry solids represents the *water*. By carefully incinerating the solids to a grayish-white color the *ash* or inorganic salts are determined. In pure milk the amount ranges from 0.7 to 0.8 per cent. A watered milk will show a reduced amount both of solids and of ash.

Determination of Fat (*Werner-Schmid Process*).—This is an easy and quite accurate method. Into a long test-tube with a capacity of 50 c.c., and graduated to show cubic centimeters in tens, measure 10 c.c. of milk and 10 c.c. of strong hydrochloric acid. (A large common test-tube can be used, and the measurement made by pipets or other graduated glasses.) The mixture of acid and milk is boiled one and one-half minutes, or the tube may be corked and heated in a water-bath for five or ten minutes, until the liquid turns a deep brown, but not black. Having cooled the tube and its contents in running water, 30 c.c. of well-washed ether must be added, the tube corked, the mixture well shaken, and finally stood aside. When the line of separation between the ether and acid is distinct, a wash-bottle cork stopper with its tubes is substituted for the plain stopper (see Fig. 93).

The lower end of the exit tube has a short curve, which is adjusted so that its opening is just above the line of separation. A weighed flask or beaker is held so as to receive the ethereal layer when it is blown out by the lips at the upper tube. In succession two additional portions of washed ether, 10 c.c. each, are shaken with the acid and blown out into the weighed flask. The ether is then distilled off or evaporated, and the fat residue dried in a water oven and weighed. It is the amount contained in 10 c.c. of milk.

Babcock's Method with Centrifuge.—For separation of fat from either human or cows' milk the graduated milk bottle (Fig. 94) may be used with any medical centrifuge (p. 591). It gives results accurate to within 0.2 per cent. of fat. It is a simple method and the manipulation is easy.

Two pipets are supplied with the bottles, one of 5 c.c. capacity; the other holding 1 c.c. up to a mark on the lower stem, for introducing the alcoholic solution.

To determine fat by this method the sample, well mixed, should be taken from the middle portion of the nursing or milking—as the first milk is poorer and the last richer than the average. Five cubic centimeters of the sample are introduced into the milk bottle by means of one pipet; 1 c.c. of alcoholic solution (which consists by volume of amyl alcohol, 37; wood alcohol, 13; hydrochloric acid, 50) is added by the other, and the bottle shaken by hand. Then by means of the large pipet strong sulphuric acid, specific gravity 1.83, is added little by little, with shaking, until the bottle is filled to the brim. When whirled in the centrifuge two minutes, the fat rises to the neck in a clear yellowish layer, and can be read off in direct percentages. If the level of the

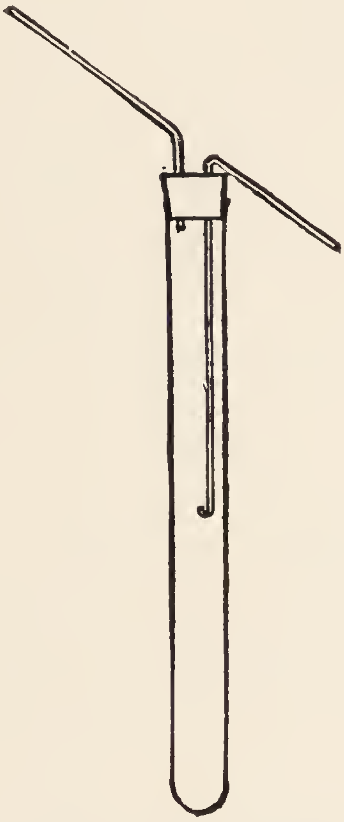


FIG. 93.—Werner-Schmid process.

FIG. 94.—Milk bottle for centrifuge.

FIG. 95.—Pipet for milk.

fat should be below the zero point as the result of the cooling, a few drops of water should be added to raise it. Another whirl of the centrifuge will carry the water below the fat layer and lift the latter to the desired point. If the milk should be richer than 5 per cent., add 5 c.c. of water to 5 c.c. of milk, mix thoroughly, take 5 c.c. for analysis, and multiply the result by 2.

For cream add 20 c.c. of water to 5 c.c. of cream, mix, take 5 c.c. for analysis, and multiply the result by 5.

The alcoholic solution can be kept some weeks. If it turn dark, a fresh mixture must be made.

By Weighing.—To determine the butter by the gravimetric

method, 10 gm. of milk are weighed into a tared dish containing a weighed amount of dry sand. The milk is evaporated on a water-bath and last on a water-oven, with constant stirring. The residue is washed a number of times with warm ether or petroleum naphtha of specific gravity 70° Baumè, and the washings passed through a small filter. The filtrates are all received in a tared beaker and carefully evaporated to a constant weight. The residue is *fat.* This subtracted from the amount of total solids gives the *solids not fat.*

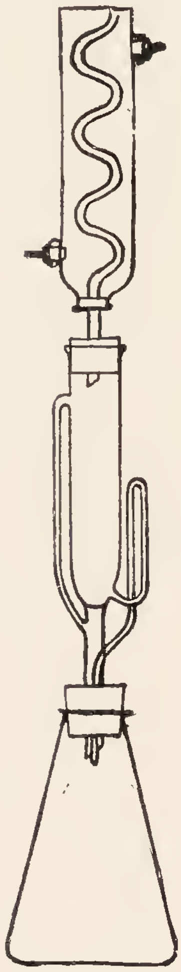


Fig. 96.—Soxhlet extractor.

Adams' Method.—This is the standard process in use by official chemists who have well-equipped laboratories. The milk is absorbed by strips of pure, fat-free paper, which distributes the milk-fat in a thin layer. The coiled strip is dried in a water oven, and then placed in the middle chamber of a Soxhlet extractor (Fig. 96). The tared flask, containing 75 c.c. of ether, is heated on a water-bath.

Ether vapor condenses in the upper apparatus, flows back upon the coil of paper, and returns to the flask. After ten such washings the flask containing the ether is detached and connected with a condenser. After distillation, the fat residue is dried in an air oven, cooled, and weighed.

PRACTICAL URINARY EXAMINATION

Ordinary Examination.—As this section is concerned with the knowledge which has value to the medical practitioner, it is deemed best to limit its range to those points which have practical significance.

A good working plan for the ordinary analysis need not include more than the following procedures, and in most cases less than the total of these will serve every requirement:

Measurement of the daily quantity.

Noting the color: if deep yellow, green, or brown, testing for biliary pigment; if reddish, smoky, or chocolate-hued, testing for hemoglobin. (Plate 7.)

Taking the reaction.

Determination of specific gravity with the hydrometer.

After the sediment falls, decanting the clear part and examining for albumin by boiling and by adding acid—nitric, picric, or acetic. If greenish flakes form, bile pigment is to be looked for; if red-brown, then hemoglobin. After twenty-four hours noting the height of albuminous layer.

Testing for glucose by Fehling's and by Böttger's methods, with calculation of the amount.

Estimation of the relative amount of chlorids.

Estimation of the amount of urea.

Noting the naked-eye appearance of the deposit which forms on standing for several hours. Making allowance for the light cloud of epithelial débris sometimes found in health, a sample voided turbid and acid points to urates or mucus or pus or blood; if voided turbid and alkaline, it points to phosphates. (Plate 7.)

Careful examination of the deposit with the microscope, using a $\frac{1}{4}$ or $\frac{1}{5}$ objective and an eye-piece giving a magnifying power of about 250 diameters. The search should be made for phosphates, calcium oxalate, uric acid, urates, epithelium, pus, tube-casts, spermatozoids, blood-cells, leucin, tyrosin, cystin, organisms such as sarcinæ, the molds, and bacteria; and in addition such extraneous substances as sometimes enter the bladder by fistula from the rectum.

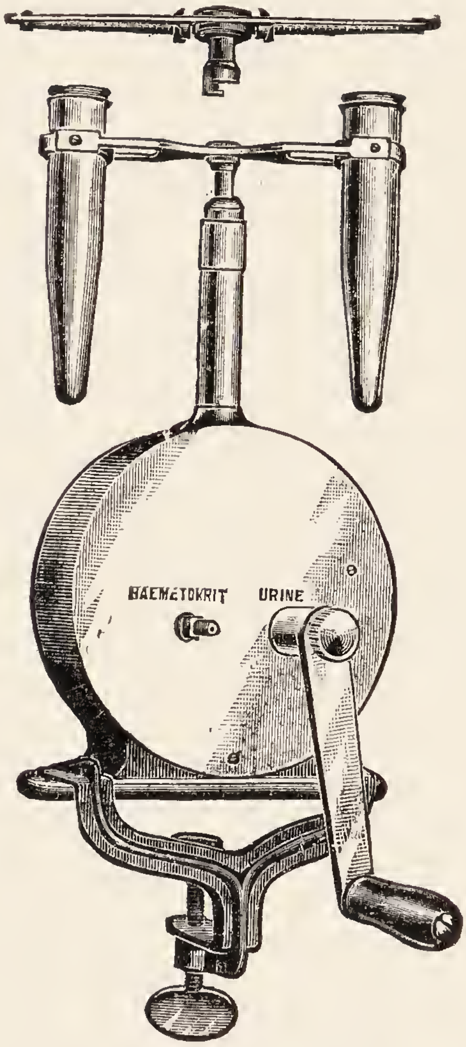


Fig. 97.—Hand centrifuge.

For minute study of the bacteria it is necessary to stain the sediment and use the high power of 900 diameters obtained with immersion lenses. The illumination should be by substage wide-angle condensers. If the absence of organic or definite crystalline structure leave a doubt as to the nature of a deposit, the following simple tests may prove serviceable: First, warm a portion of the deposit with some urine in a test-tube: if it clear up, then the urates are present; if it do not clear up, then suspect phosphates. Second, warm a fresh portion with acetic acid: if it dissolve, phosphates are present.

Precautions as to the Sample.—The microscope often shows substances which, being extra-urinary, may be broadly described as dirt, having no significance whatever. Owing to ignorance or carelessness on the part of patient or nurse, it not infrequently happens that floating dust or sweepings or fecal matter get into the vessel, or sometimes an unclean bottle may make its contribution. Hairs, cotton, and linen fibers may be mistaken for tube-casts, while such objects as large globules of free oil, starch granules, and vegetable cells are obviously extraneous. To avoid fallacies it is well to enjoin care upon the patient or nurse to have the container sterilized by a hot solution of calx

chlorinata. The urine should be voided into a well-cleaned chamber-vessel, or, better still, into a glass collecting-jar sufficiently large to hold the entire daily amount. By means of a clean glass funnel about 8 fl. oz. should be transferred to a bottle or, if in hospital, to a conic glass.

Before taking up a drop of the deposit with the pipet, for examination with the microscope, sufficient time must be allowed for the sediment to collect. As a rule, this will require that the sample should stand for about three hours, but if rotated in a centrifuge, separation will occur in three minutes. If the amount of the spontaneous deposit be small, it can be concentrated by decanting the clear fluid and using the centrifuge upon the sedimentary portion.

To get the best results from the centrifuge the bearings should be lubricated, violent rotation avoided, and the arms balanced by carrying equal loads of the fluid. The readiness with which urine undergoes change is a noteworthy fact. The liability varies in different specimens. Even a healthy urine may in a few hours after micturition increase in acidity, owing to the change of the common soluble urates to the more acid and less soluble salts, which are precipitated along with more or less free uric acid.

$$\underset{\text{Acid phosphate.}}{2(NaH_2PO_4)} + \underset{\text{Sodium urate.}}{Na_2H_2C_5N_4O_3} = \underset{\text{Neutral phosphate.}}{2(Na_2HPO_4)} + \underset{\text{Uric acid.}}{H_4C_5N_4O_3}$$

The destiny of the urea in all specimens kept several days in a warm place is to be converted into ammonium carbonate by the growth of the *Micrococcus ureæ* and its enzym, *urase.*

$$\underset{\text{Urea.}}{CO\,.\,N_2H_4} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Ammonium carbonate.}}{(NH_4)_2CO_3}$$

This change may take place in the bladder if the urine be retained too long, and may cause grave complications in vesical diseases.

The urine itself becomes turbid, putrid, and irritating, throwing down a deposit of phosphates with urate of ammonium.

$$\underset{\text{Ammonium carbonate.}}{(NH_4)_2CO_3} + \underset{\text{Magnesium phosphate.}}{2MgHPO_4} = \underset{\text{Ammoniomagnesium phosphate.}}{2(MgNH_4PO_4)} + H_2CO_3.$$

To correct this tendency in cases of cystitis it is customary to wash out the bladder with a saturated solution of boric acid or some other unirritating antiferment.

Preservative Fluid.—The sample of urine should be examined within twelve hours after micturition, and preferably within three hours, merely allowing time for the deposit to settle. When it is desired to preserve a specimen for several days, it suffices to add 5 drops of chloroform or 1 gr. of thymol to 1 fl. oz.,

or salicylic acid, about 3 gr. to ½ pt. of urine. This will not prevent the changes of structure which sometimes take place in blood-cells, tube-casts, and renal epithelium when the urine is of low density. To protect these from alteration the density must be raised by adding some mineral salt, such as potassium acetate, in saturated filtered solution containing a few grains of salicylic acid. A sediment can be preserved indefinitely by first giving it several washings in a solution of chloral, 15 gr. to 1 fl. oz. of water, and finally setting aside, covered with the same solution. The chloralized specimen can be mounted permanently for the microscope. Chloral and chloroform each reduces Fehling's solution, so thymol should be used to preserve if the urine is to be tested for glucose. Thymol may mask albumin as it precipitates white with nitric acid. Boric acid is a good preservative, in the proportion of 5 gr. to 4 fl. oz. of urine. Formaldehyd, 1 drop, will preserve a pint of urine one week, but it coagulates albumin if care is not observed, and it reduces Fehling's solution.

Another method of preserving organized sediments is to wash three times with normal salt solution, and, after decanting, put the sediment in equal parts of glycerin and water with 2 per cent. of saturated alcoholic solution of thymol.

Normal Urine.—The urine of health is a clear solution in water of various substances. Some of these impart a freely acid reaction; some give it a yellowish color; some are the source of its characteristic odor; and all combined raise its specific gravity to a point between 1015 and 1025. The proportion of its constituents are not constant for all individuals, nor even for the same person taking one day with another; indeed, they vary hourly. In making a statement of average composition, regard is had to this variable character: the figures which follow may be taken as representing the average amounts in round numbers.

Average composition of normal urine.	Percentage Composition.	Grains per diem.	Grams per diem.
Water	96.0	50 fl. oz.	1200 c.c.
Solids as tabulated below	4.0	1000 gr.	60 gm.
Urea	2.000	500	30.00
Uric acid	0.040	10	.65
Hippuric acid	0.075	15	.95
Creatinin	0.075	15	.95
Pigment, mucus, xanthin, other extractives, etc.	1.000	170	10.00
Chlorids of potassium and sodium	1.000	170	10.00
Sulphates of potassium and calcium	0.110	40	2.60
Phosphates of potassium and sodium	0.120	45	2.90
Phosphates of magnesium and calcium	0.080	30	1.95

Besides these, there have been found traces of indican, phenol, and other aromatic sulphates, diastase, oxalic, and lactic acids, unoxidized sulphur, and phosphorus.

The Quantity.—In making a quantitative determination of any constituent, not only must the tested sample be a portion taken from the total mixed urine of the day, but the daily quantity of the urine itself must be known. The large collecting-jar may be graduated so as to be the measuring vessel: such wide-mouthed graduated jars as are used by druggists for percolating will serve admirably, though the common glass *specie jar* is about as good, and is easily obtained anywhere. It must be large enough to hold the entire daily discharge, and then for measuring the volume a smaller apothecary's graduated glass can be used. The wide mouth admits of the introduction of the hand for the thorough washing always required before beginning the daily collection. The patient is instructed to empty his bladder at a given hour, but not into the jar. Afterward, for twenty-four hours, the urine is passed into the one jar, which should be kept in a cool place, and at the given hour the last contents of the bladder are added to it. The amount should then be noted, and about 8 fluidounces put into a perfectly clean glass bottle or other vessel to serve as a sample for analysis.

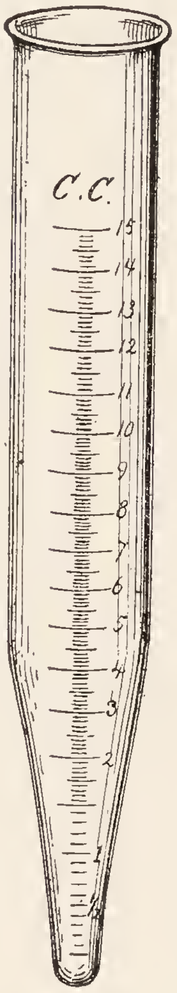


Fig. 98.—Percentage tube.

Practical Import.—The mean daily discharge is 1250 c.c., or 50 fl. oz., or 3 pints. In drawing conclusions from any change in this respect, it is necessary first to note that even in health there may be considerable variation. The amount voided will depend, first, upon the amount of water drunk; it will be affected by the proportion of water lost in perspiration and the quantity retained in the tissues as necessary for nutrition. These factors are various in different men, and change with the season and with the habit of exercise. It is compatible with health in some for the daily discharge to reach only 1½ pints, and at times for it to go as high as 4 pints. Making allowances for these physiologic variations, the urine is notably scanty in certain forms of Bright's disease, in cirrhosis of the liver, and in the state of collapse occurring in cholera or the pernicious fever.

By *anuria* is meant a condition in which the urine is no longer voided: this includes *suppression*, when the secretion of the kidney is suspended, and *retention*, when the fluid, although secreted, is retained in the urinary passages by mechanical obstruction. *Oliguria* is the term applied to urine scanty from low pressure of the blood or other cause.

A persistent excess of the aqueous constituent, without a cor-

responding increase of the solids, is termed *hydruria*. This symptom is characteristic of diabetes insipidus, in which disease the daily discharge may be more than 8000 c.c., or 2 gal., while the specific gravity sinks to 1003 or less. Some diuresis occurs in the middle period of atrophic nephritis. Hysteric and neurotic subjects may suffer temporarily from a too copious urinary flow.

By *polyuria* is meant an excess not only of urinary water, but of all the solid constituents. Beside the saccharine diabetes, it would include cases of *azoturia*, in which the urea is morbidly abundant, and the *phosphatic diabetes* of Teissier, which accompanies an excessive tissue-waste.

Phthalein Test (p. 471).—To learn the functional activity of the kidneys, after giving the patient 300 c.c. of water, the bladder is emptied and a sterile solution of phenolsulphonephthalein as the monosodium salt, .006 gm. in 1 c.c., is injected into the muscles of the arm. Normally, the dye begins to be excreted in from five to ten minutes and almost all passes the kidneys within two hours. As the urine is secreted it drops into the collecting glass, which has in it a few drops of 25 per cent. sodium hydroxid. As soon as the alkalized urine turns reddish excretion of the drug has begun. Delay beyond ten minutes means functional derangement of the kidneys. Estimates can be made of the percentage by alkalizing and testing with a Hellige or Duboscq colorimeter the samples collected at the ends of the first and the second hour. Normally, 38 to 60 per cent. of the drug is excreted during the first hour and 60 to 80 per cent. in the second. The color standard is .003 gm. of the phthalein to 1 liter of water alkalized by sodium hydroxid. If the reading of the colorimeter is 20, then there are 50 per cent. present of the .006 gm. administered. In the absence of a colorimeter, comparison may be made with the pink color in a set of tubes of known percentage content.

Clinical Import.—The amount of this drug excreted does not correspond to the volume of the urine. Though the quantity of liquid be normal, the permeability to the drug may be much diminished in proportion to the intensity of the kidney mischief. Uremia may be impending in nephritis or the puerperal state when the liquid output is normal in volume.

The Color.—Normal urine is amber-hued, the depth of color varying as the proportion of coloring-matter varies. When the volume of urine is low, the liquid is dense and the color deepens to a reddish tint. After liberal drinking, followed by copious urination, it may be almost as colorless as water itself.

Beside its true coloring principles—*urobilin*, *urochrome*, *hematoporphyrin*, and *uro-erythrin*—the urine contains sulphindoxylate of potassium or *indican* ($KC_8H_6NSO_4$), a colorless

substance which forms indigo-red or indigo-blue by the action of reagents.[1] Its presence may be shown by Jaffé's test for indican: add to two inches of urine in a test-tube an equal volume of fuming yellow hydrochloric acid and one or two drops of liquor sodæ chlorinatæ or three drops of solution of hydrogen dioxid, or (the author's modification) a piece of sodium perborate (Schering) as big as a pea. There is danger of carrying oxidation too far, changing the indigo-blue to yellow isatin. The sodium perborate is less likely to do this than the chlorinated soda or chlorinated lime. It is very stable in all climates and always ready for use, which can not be said of either of the chlorinated preparations or the hydrogen dioxid. On standing, the mixture turns bluish from the formation of indigo. The color may be concentrated by gently shaking with 1 c.c. of chloroform or of ether for two minutes; the indigo is taken up by it and on standing separates as a layer which is blue in color in proportion to the amount of indican. (Plate 8, Fig. 8.) With normal urine there is a pale blue color. Diseases of the liver and bowels which cause constipation thereby favor the absorption of indol from the fecal mass, and an increase of its derivative, indican, in the urine. This increase is revealed by the deeper color yielded when the above test is applied. A fallacy results if iodids are present through ingestion, as the free iodin dissolved in chloroform gives a rose violet color. Iodin in the ether layer would be brown and at the surface (p. 145).

The urine is pale yellow in the free flow of diabetes and after attacks of hysteria or epilepsy; orange red from the elimination of santonin in an alkaline medium; reddish naturally after full meals with small potations, after severe exercise with abundant sweating, during paroxysms of fever, after hemorrhage into the genito-urinary tract, and, lastly, after the administration of logwood; brownish from the condition known as melanosis, from hemoglobinuria, and from the administration of tar, carbolic acid, gallic acid, tannic acid, senna, trional, or sulphonal. Eating of blue candies and the administration of methylene-blue for gonorrhea will cause green urine. In jaundice the biliary coloring-matter (*q. v.*) will make it sulphur yellow or olive-green.

Practical Import.—It is plain that excess of indican would point to diseases retarding digestion or causing constipation, though it has been found in cholera and all forms of severe cachexia. The detection of foreign coloring-matter would furnish indications of an obvious character based upon the nature of the specific

[1] *Artificial indicanuria* can be made by adding to normal urine horses' urine, or an alcohol extract of its solid residue. The urine of the horse, rich in indican, can be kept ready for use by adding to it chloroform, five drops to the fluidounce.

substance: for that of blood consult the section on Hematuria; for that of bile, the section on Biliary Coloring Matter (p. 569).

Urorosein is present as a chromogen in very small amount in normal urine. The amount is increased in advanced tuberculous disease, malignant diseases of the abdominal organs, typhoid fever, anemia, and diabetes. It changes to a rosy red pigment after the addition of an oxidizer, such as nitric acid, as a test for albumin. When the rosy tint spreads through the column of urine in Heller's test for albumin, an excess of urorosein is present. It can be distinguished from indigo-blue by its not separating after being shaken with chloroform.

Alkaptonuria.—A peculiar dark-brown color has been observed in the urine of certain persons and certain families. It is attributed to the presence of *alkapton*, which in the air oxidizes to a darker substance. In recent years cases have been reported which appear to be congenital. They could not be accounted for by special foods or medicines or diseases, the condition appearing to persist through life as an inherited anomaly of nutrition. The latest view is that the material of alkaptonuria is a substance called *homogentisic acid* or hydroquinone-acetic acid, $C_6H_3(OH)_2CH_2COOH$, which is occasionally mixed with *uroleucic acid.* The urine containing them becomes dark-colored when made alkaline with sodium or potassium hydroxid and shaken for a few seconds, or merely on exposure to the air, and it reduces Fehling's solution. Homogentisic acid is formed in the small intestine as a cleavage product of the protein molecule, but that found in the urine is due to a specific derangement of protein metabolism.

Specific Gravity.—When it is desired to make use of this property in determining by special formulas the amount of urea or of sugar in solution, it is best to take the observation with a delicate Mohr balance or with the specific-gravity bottle. A bottle of known capacity, say of 1000 gr., is counterpoised, then filled with urine, and weighed in a delicate balance. If the contents weigh 1025, that number will be the specific gravity. This operation requires apparatus not always at hand, and consumes time not always at the disposal of the physician. For ordinary purposes it suffices to take the specific gravity with a *urinometer*, which is a spindle hydrometer for liquids heavier than water, carrying a scale ranging from 1000 to 1060, and usually made to read at 25° C. (77° F.). When the sample of urine is too small in amount to use the urinometer, the specific gravity of 1 c.c. can be taken by the method described under the section on Specific Gravity (p. 24).

Method.—Fill to one-half its capacity a cylindric vessel having a level lip. Gently immerse the urinometer and carefully fill the

cylinder to the brim. Take the observation by sighting on a level with the surface of the urine, which rises slightly above the edge of the glass. Note the lower surface line and not the point to which the liquid is attracted up the side of the scale.

Practical Import.—The standard of health is usually rated as between 1015 and 1025, but very free use of beverages may cause it to fall below 1010. Under ordinary conditions, in regard to the amount of fluid ingested, so low a density would point to diabetes simplex or to Bright's disease with deficiency of urea. When the record is above 1030, it usually denotes sugar in the urine. In either case the proper chemical tests would solve the doubt.

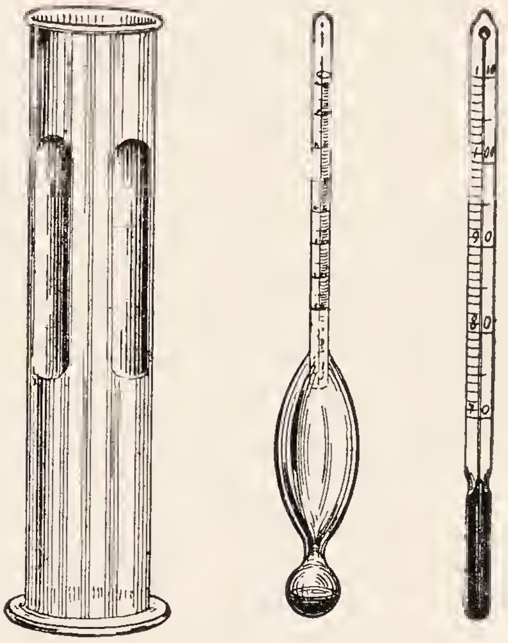


Fig. 99.—Squibb's urinometer.

Total Solids.—It is possible to derive valuable conclusions from roughly estimating the solid constituents of the urine by multiplying the last two figures of the specific gravity with Haeser's factor, 2.60. This gives parts of solids per thousand of urine, and after measuring the number of liters passed in twenty-four hours, furnishes some idea of the efficiency of the kidney at the time. Another rule giving grains of solids is to take the total number of fluidounces passed in the day, multiply by the two last figures of its specific gravity, and add 10 per cent. Thus if 50 fl. oz. be passed, the specific gravity being 1015, the total solids are found by $50 \times 15 = 750$ and $750 + 75 = 825$ grains. The average amount excreted daily by a healthy male is 70 gm., or 1100 grains.

Cryoscopy.—The determination of the freezing-point, lowering of the urine as evidence of the molecular concentration, is a help to which reference has been made in another place (p. 39). The method is invested with so many technical difficulties that the practical physician contents himself with deducing the activity of the kidneys in this respect empirically by multiplying the last two figures of specific gravity carried to the third decimal place, by factor 0.075° C. The sample must be free of sugar and albumin. Thus, if the specific gravity carefully taken gave the last two figures and decimal as 10.125, then $10.125 \times 0.075 = 0.759°$ C., which is less than the normal range (1.2 to 2.3).

Reaction.—In noting the reaction blue and red litmus-papers may be used, but the most convenient indicator is violet-colored *neutral* litmus-paper. Acids turn it red and alkalis blue. A

sample of the total daily urine of health should turn this neutral paper, or even the blue paper, to a delicate red. This shows an acid reaction due to the hydrion dissociated from various acid radicals largely organic in character.

Occasionally a sample is encountered which turns blue litmus red and red litmus blue. It is said to have an *amphoteric reaction*, due to the fact that the urine contains both the acid hydrion and the alkaline hydroxidion in small amounts.

Test for Acidity.—Having measured into a 200 c.c. flask 25 c.c. of urine, add 15 to 20 gm. of powdered neutral potassium oxalate and 1 or 2 drops of a 1 per cent. phenolphthalein solution. Shake the mixture well for one to two minutes and titrate it immediately with $\frac{n}{10}$NaOH until a faint but permanent pink remains after further shaking. Acidity is expressed in terms of oxalic acid, of which 0.0063 gm. equals 1 c.c. of the decinormal sodium hydroxid. If 3 c.c. of the soda neutralize 25 c.c. of the urine, then the acidity of 100 c.c. is $3 \times 4 \times 0.0063 = 0.0756$, which is the same as 0.756 parts per thousand. Further details are given under Acidimetry (p. 124). The neutral potassium oxalate is used to get rid of disturbing factors by precipitating the calcium and magnesium salts as oxalates.

Sometimes in health a sample representing the unmixed urine secreted during the first or second hour after a full meal is alkaline or neutral, as an effect of the preponderance of alkaline salts in the food. The paper made blue by such a sample retains the blue color, thus indicating *fixed alkali*—that is, alkaline salts of sodium and potassium.

The same change can be produced at will by the repeated administration of large doses of the bicarbonates or citrates of sodium and potassium, as in the alkaline treatment of rheumatism. When the paper is turned blue by the *volatile alkali* ammonia, we may know it by the gradual restoration of the original color as the ammonia volatilizes. A characteristic putrid odor attends this reaction. It is due chiefly to the ammonia evolved from ammonium carbonate resulting from the decomposition of urea by the *Micrococcus ureæ*.

$$\underset{\text{Urea.}}{CON_2H_4} + \underset{\text{Water.}}{2(H_2O)} = \underset{\text{Ammonium carbonate.}}{(NH_4)_2CO_3}$$

Practical Import.—Persistent alkalinity due to fixed alkali is sometimes found in persons of a feeble habit of body. The change in reaction lessens the solvent power of urine for the earthy phosphates, which in consequence are precipitated in loose whitish amorphous particles. These do not tend to form concre-

tions. If the alkalinity be due to ammonia, the indication is very different. The ammoniacal change occurring in the bladder is a concomitant of serious vesical mischief. The earthy phosphates are mixed in a deposit with the *triple phosphates* of ammonium and magnesium. If the bladder be not kept well washed of this deposit, it will in time accrete into the *mixed phosphate* gravel or calculus. In every case of incomplete evacuation of the bladder from paralysis or obstruction this is a rock ahead.

It remains to be said that the administration of acids, unless it be benzoic acid, which is changed to hippuric acid, while tending to acidify the urine, will have little direct effect upon the reaction. The strongest acids, given in usual doses, are neutralized before they enter the circulation. Whatever power they have over the alkaline urine of feeble subjects is explained by the increased tone they impart to digestion, thus removing debility and anemia. Given by the mouth, they exert no control over ammoniacal urine.

Urotropin is given to check the ammoniacal fermentation, which it does by liberating formaldehyd in the urinary passages. Doses of acid sodium phosphate (NaH_2PO_4) given at the same time are eliminated by the kidneys and will lower the alkaline reaction by neutralizing the ammonia in the urine.

Phosphates.—The urinary phosphates may be divided into two groups, earthy and alkaline, according to their bases. The total daily discharge of these is about 60 gr. or 4 gm., the two phosphates of calcium and magnesium, or *earthy* ($MgHPO_4 + Ca_3(PO_4)_2$), constituting one-third, and the acid sodium and potassium phosphates, or *alkaline* ($NaH_2PO_4 + KH_2PO_4$), the other two-thirds. The presence of both groups is shown by the following procedures:

To the urine in a test-tube add a few drops of potassium hydroxid and boil. The earthy phosphates are thrown out and must be separated by filtration. Then to the filtrate add one-third its volume of *magnesia mixture*. The precipitate formed represents the phosphoric acid once held by alkaline bases, now in the form of ammoniomagnesium phosphate (triple phosphate).[1]

In order to estimate approximately the total phosphoric acid, resort may be had to *Teissier's method*. All the apparatus needed is a glass cylinder graduated in the cubic centimeters of the metric system. Put into the graduate 50 c.c. of urine and add 15 c.c. of magnesia mixture (magnes. sulph., parts 10; ammon. chlor., 10;

[1] *Artificial phosphatic urine* (for students' practice) which becomes turbid on boiling can be made by adding and shaking with it freshly precipitated calcium carbonate. Part of it dissolves; the rest can be filtered off. The calcium carbonate can be obtained from a strong solution of calcium chlorid by the addition of sodium carbonate, leaving the calcium chlorid solution in excess to be filtered off.

aq. ammon. fort., 10; water, 80). Shake well and set aside for twenty-four hours. All the phosphoric acid is thrown down as ammoniomagnesium phosphate, a dense white deposit. At the end of twenty-four hours note the number of cubic centimeters occupied by this sediment. For 1 c.c. there are 0.3 gm. per liter, or 0.03 per cent. of phosphoric acid, equivalent to 0.6–0.7 gm. of phosphates per liter, or 0.06–0.07 per cent. To obtain a result in terms of grains to the fluidounce multiply by 4.55.

The **centrifuge determination** by volume is made by filling the percentage tube with urine to the 10 c.c. mark and adding 5 c.c. of magnesia mixture. After rotation for three minutes the precipitate falls in a compact stratum, every $\frac{1}{10}$ c.c. of which is read as 1 per cent. of phosphates by bulk. The phosphate precipitate of normal urine is about 8 per cent. by bulk. Each $\frac{1}{10}$ c.c. of the sediment is estimated to equal 0.0225 per cent. by weight of P_2O_5. Purdy prefers 10 c.c. of urine, 2 c.c. of 50 per cent. acetic acid, and 3 c.c. of uranium nitrate (100 gr. to 4 oz.). Invert several times, stand aside three minutes, then rotate three minutes at 1200 revolutions per minute. Read off bulk per cent. of $H(UO_2)PO_4$, of which $\frac{1}{10}$ c.c. $= P_2O_5$, 0.04 per cent., or 0.19 gr. to 1 fl. oz.

Volumetric Method.—For more accurate calculations the volumetric method will serve. The standard solutions used and the indicators can be had of all first-class druggists, who keep formularies in which the mode of preparation is given. Put 50 c.c. of urine into a porcelain capsule, and add 5 c.c. of a saturated solution of sodium acetate containing an excess of acetic acid. Heat on a sand-bath or wire gauze until boiling begins, and then from a buret slowly add about 2 c.c. of standard solution of uranium acetate, causing a precipitate of uranium phosphate. Stir with a glass rod, and touch its wet end to a drop of solution of potassium ferrocyanid on a white plate. A red-brown color indicates that too much standard solution has been used, and the process must be repeated. However, this is not likely when only 2 c.c. have been used. If no red-brown spot appear, continue to add from buret slowly, and after the addition of each 1 c.c. stir and touch the rod to the ferrocyanid. When the red-brown spot appears, read off the number of cubic centimeters taken from the buret. The standard solution contained 31.1 gm. of uranium acetate to 1000 c.c. of water, equal to 5 gm. of phosphoric acid (P_2O_5). If 1000 c.c. $= 5$ gm. P_2O_5, then 1 c.c. will represent 0.005 gm. P_2O_5 in the 50 c.c. of urine employed. The terms in percentage can be obtained by multiplying the number of cubic centimeters used by 0.01, which is the equivalent of 0.005×2. To get grains to the fluidounce multiply the per cent. by 4.55.

Practical Import.—When it is considered that the phosphates of the urine are derived only in part from the waste of nervous tissue, part being supplied by the rest of the body, and an uncertain amount coming almost directly from the same principles in food, it will be easily understood why the quantitative estimates so far have proved of no direct value to the clinician. Their significance depends not on the relative proportion in the sample, but upon their state. Any amount, large or small, in an undissolved state will figure as a deposit, and thereby have pathologic meaning (Pl. 7, Fig. 2).

Phosphatic Deposits.—It has been said above that the phosphates of normal acid urine are held in clear solution. When the urine is alkaline, it loses its solvent powers for the earthy

Fig. 100.—Triple phosphate and spheres of ammonium urate.

phosphates, and throws them down as a grayish-white sediment made of colorless granules, which show no tendency to aggregate into masses having particular shapes. The amorphous urates form into groups which branch somewhat like sprigs of moss. A drop of acetic acid insinuated under the cover-glass will clear away the phosphates, but not the urates. If the alkalinity be due to the ammoniacal fermentation of urea, then the ammonia reacts with the magnesium phosphate to produce the white crystalline deposit of ammoniomagnesium phosphate—the so-called *triple phosphate.*

$$\underset{\text{Magnesium phosphate.}}{2MgHPO_4} + (NH_4)_2CO_3 = H_2CO_3 + \underset{\text{Triple phosphate.}}{2MgNH_4PO_4}$$

PLATE 7.

URINARY SEDIMENTS.

The most important macroscopic varieties of urinary sediment are represented in the three conical glasses.

FIG. 1. **Brick-dust Sediment.**—This is formed only of uric acid, and is found in abundance in febrile states, after active bodily exertion, etc. It dissolves on heating.

FIG. 2. **Yellowish Friable Sediment.**—This may consist of phosphates (soluble on addition of acid), of pus-corpuscles, of renal elements, of bacteria (demonstrable microscopically).

FIG. 3. **Bloody Sediment.**—Demonstrable by Heller's blood-test (see Plate 8, Fig. 10), as well as by microscopic examination (renal or vesical hemorrhage, hemoglobinuria).

Uric-acid Sediment.

FIG. 4. **Sodium Urate**, in small yellowish granules, frequently adherent to other elements, especially casts, etc.

FIG. 5. **Uric-acid Crystals**, varying in color from yellow to yellowish-brown, in large, not entirely regular plates, in whetstone, dumb-bell, and comb-like form and arrangement.

Both sediments occur only in urine of acid reaction, and are precipitated by addition of acid. They dissolve upon addition of potassium hydroxid.

(JAKOB.)

PLATE 7.

Usually the crystals are large enough to be seen by the naked eye as minute glittering points, which the microscope resolves into large, bright triangular prisms or modified forms, sometimes feathery and sometimes having a resemblance to a *coffin-lid* (see Fig. 100).

The existence of these mixed phosphates as a spontaneous deposit at the time of micturition usually indicates some serious bladder trouble, such as cystitis or paralysis or stone. Incomplete evacuation of the bladder has favored the ammoniacal fermentation in the retained urine. If the condition persist, there is ground to fear that eventually a phosphatic concretion will form in the bladder and in the pelvis of the kidney.

Stellar calcium phosphate is sometimes deposited in urine which is alkaline from fixed alkali, and is rarely seen except in some

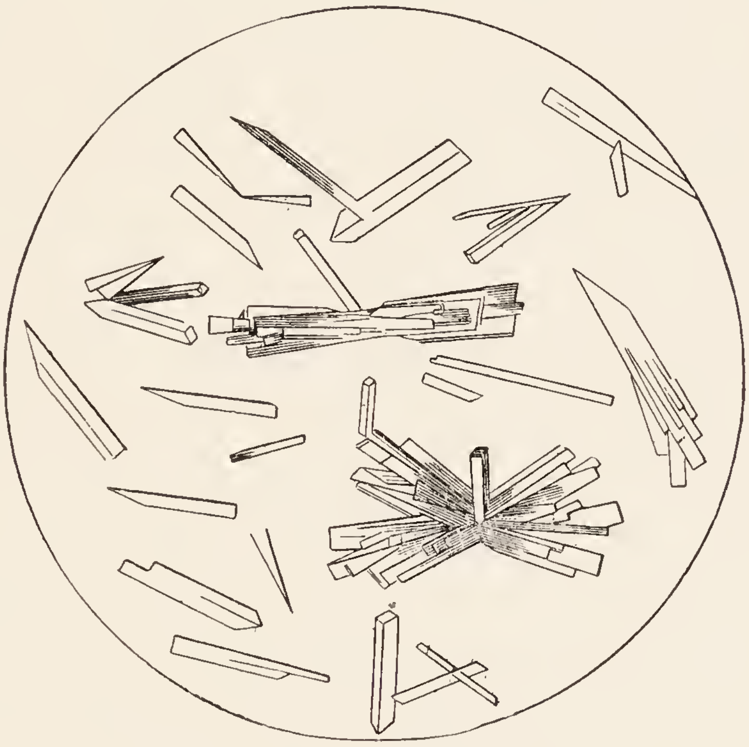


Fig. 101.—Stellar calcium phosphate.

general disorder of serious import. Commonly it occurs in arrowheads or slender wedges, singly or gathered in star-like masses (see Fig. 101).

Sulphates.—Sulphuric acid is present in the urine partly as preformed *mineral sulphates*, and partly as compounds conjugated with phenol, indol, and skatol, known as *ethereal* or *aromatic sulphates* (p. 431). The sulphates of the alkaline metals and magnesium ($K_2SO_4 + Na_2SO_4 + MgSO_4$), which are eliminated by the urine to the extent of about 2 gm. or 30 gr. daily, are derived chiefly from the diet and partly from the oxidation of the protein principles of the tissues and fluids.

These mineral salts make up nine-tenths of the total sulphates; the remaining one-tenth is in the form of *ethereal compounds* of con-

jugate acids, such as the phenol-, cresol-, indoxyl-, and skatoxyl-sulphates of potassium. These are products of protein putrefaction, absorbed from the intestines and eliminated by the kidney. Their normal amount varies between 0.12 and 0.3 gm. Any increase is roughly indicative of intestinal indigestion (p. 596).

Determination of Total Sulphates.—Mix urine, 100 c.c., with 20 c.c. of 5 per cent. barium chlorid and 10 c.c. of hydrochloric acid. Boil half an hour; filter the white precipitate of barium sulphate; collect, dry, and weigh. For 100 parts of the $BaSO_4$ calculate 42 parts of absolute H_2SO_4, or 34.3 parts of sulphuric anhydrid, SO_3.

Determination of Ethereal Sulphates Only.—These can be determined by the following procedure: Take of urine 200 c.c. and mix with an equal volume of barium chlorid made alkaline with barium hydrate. Filter off the precipitate through dry paper. The clear filtrate contains the ethereal sulphates, which are not precipitable by barium chlorid until they are decomposed by boiling with hydrochloric acid. Take 200 c.c. of this filtrate, representing 100 c.c. of urine and 20 c.c. of hydrochloric acid, and boil ten minutes. Filter, dry the precipitate, and calculate H_2SO_4 as stated above. The easiest clinical test is the one known as *Jaffé's test* for indican (see Indican, p. 595). In general the indican reaction is deep in color in proportion to the total excretion of ethereal sulphates (p. 493).

Centrifuge Estimation of Mineral Sulphates.—Into the graduated tube put 10 c.c. of urine and 5 c.c. of barium chlorid solution ($BaCl_2$, 4 parts; HCl, 1 part; H_2O, 16 parts). Invert several times, set aside for three minutes, and rotate three minutes. Read each $\frac{1}{10}$ c.c. of sediment as percentage by bulk, the normal amount being 0.8 per cent. Every $\frac{1}{10}$ c.c. of sediment represents 0.25 per cent. of SO_3, or 1.1 gr. to 1 fl. oz.

Practical Import.—Although their amount is increased by fever and other wasting pathologic conditions, the increase is not strictly proportional. The effect of diet is not easily calculated, nor can exact allowance be made for the uneven action of the eliminative process. On these accounts it is of little value to the clinician to determine the amount of the mineral sulphates. When the blue indican reaction is strong, it shows that the ethereal sulphates are increased, and we find, at the same time, symptoms of impaired intestinal digestion, such as pains, flatulence, constipation. Before operation for cancer of the intestines it is desirable to know if the intestines are empty. This is indicated by the decline of conjugate sulphates in the urine to a mere trace.

Salomon-Saxl Sulphur Test for Cancer.—Dilute 150 c.c. of urine with 100 c.c. distilled water (albuminous urine must first be boiled,

treated with a small quantity of acetic acid and carefully filtered); then add 150 c.c. Salkowsky's barium solution (a mixture of 2 parts barium hydroxid solution, saturated at room temperature, with 1 part barium chlorid solution saturated at room temperature). Filter and to the clear filtrate add more reagent to insure complete precipitation. The ethereal sulphates are removed from the entire filtrate by adding 30 c.c. hydrochloric acid (specific gravity, 1.12), transferring to a 500 c.c. flask, covering with a small funnel, and heated to boiling on an asbestos mat, with a small flame, for an hour. The flask is then covered with a beaker and allowed to stand on a water-bath till the supernatant liquid is clear (requiring from four to twenty-four hours). Filter twice through a double "barium filter," small; wash the flask with sodium hydroxid solution and distilled water; boil again, using same precautions as above, and filter through a double "barium filter." (If there is still more precipitate formed, place the flask on the water-bath again.) Treat 200 c.c. of the filtrate with 3 c.c. strong hydrogen peroxid solution (perhydrol Merck) and boil fifteen minutes, covering again with the funnel, in the same flask. The liquid is poured into a sedimentation glass and observed in from one-half to four hours.

Practical Import.—In cases of cancer a decided sediment will be observed, while as a rule normal urine does not show a sediment in four hours—but some time later a trace of ethereal sulphate not properly removed as above may show.

Chlorids.—Nearly 200 gr., or 8 to 12 gm., of these salts ($NaCl$ and KCl) are discharged daily by the urine. They are greater in amount than the sulphates and phosphates together. In testing for them the sample is first acidulated with a few drops of nitric acid, so as to hold the phosphates in solution. Then, drop by drop, a strong solution of silver nitrate (ʒj–f℥j) is added so long as white curds of silver chlorid are precipitated. If the amount of chlorids is less than normal, then, instead of heavy curds being formed, the urine becomes milky or cloudy. A rough estimate can thus be made as to any marked deviations from the normal quantity.

Volumetric Determination.—This Volhard-Harvey method is based upon the test just given, using a standard solution of silver nitrate (29.06 gm. per liter, of which 1 c.c. = 0.01 sodium chlorid), and as companion the standard ammonium thiocyanate, which is reddened by the indicator, a saturated solution of ammonioferric sulphate acidified. Place 5 c.c. of urine in a small dish and dilute with 20 c.c. of distilled water. Adding 10 c.c. of standard silver nitrate precipitates the white chlorid. To this add 2 c.c. of the indicator.[1] From

[1] Made by diluting 7.0 c.c. of 33 per cent. nitric acid (specific gravity, 1.2) with 30 c.c. of water and dissolving in it 100 gm. of ferric ammonium sulphate.

a buret drop in standard ammonium thiocyanate[1] until the mixture takes a red-brown tinge, seen plainly after subsidence. This is the end of the reaction. If the red tint appears with the first drop of thiocyanate 10 c.c. more of silver nitrate must be added before completing the titration as above stated, and 20 c.c. of silver nitrate be considered in the calculation instead of 10 c.c. The calculation is made as follows: Divide the buret reading by 2, and subtract the quotient from the number of cubic centimeters of silver nitrate taken (10 or 20) in order to get the number of cubic centimeters of silver nitrate actually used to precipitate the chlorids in the 5 c.c. of urine. Since 1 c.c. of silver nitrate equals 0.01 gm. sodium chlorid, then the number of cubic centimeters of silver nitrate used, multiplied by 0.01, gives the grams of sodium chlorid in 5 c.c. of urine, and this multiplied by 20 gives percentage. The total excretion of sodium chlorid for the twenty-four hours can be readily calculated by subtracting the buret reading from 20 c.c., multiplying by the total cubic centimeters' volume of urine for the day and pointing off three decimals.

The **centrifuge determination** by volume is made with urine previously filtered or rotated until clear. The clear urine to the amount of 10 c.c. is put into the percentage tube, then acidulated with 1 c.c. of nitric acid, and finally 4 c.c. of strong solution of silver nitrate is added (ʒj–f℥j). Stand aside three minutes after several inversions. After rotating for three minutes the precipitated chlorids are read off as 1 *per cent.* by bulk for every $\frac{1}{10}$ c.c. The measure of normal chlorids is from 10 to 12 per cent.

Every $\frac{1}{10}$ c.c. represents 0.13 per cent. of NaCl by weight, or 0.62 gr. to 1 fl. oz. The normal proportion of NaCl by weight is 1 per cent.

Practical Import.—It has been observed that in acute febrile diseases, such as pneumonia, pleurisy, and rheumatism, at the stage in which exudations are forming, the chlorids are retained in the body while they diminish in the urine. In cases of pneumonia with extensive exudation they may totally disappear. Their reappearance may be expected when resolution sets in and the fever declines. The missing quantity is made up by excess in convalescence.

[1] Made by dissolving 13 gm. ammonium thiocyanate in 1 liter of water and titrated against the silver nitrate to standardize as follows: To 10 c.c. of standard silver nitrate solution in a small dish add 30 c.c. of distilled water and 2 c.c. of the acidified ferric alum indicator. Run in the ammonium thiocyanate from a buret until a permanent red-brown tinge is observed. The 30 c.c. divided by 10 gives 3, which must be multiplied by the difference between the buret reading and 20 c.c. The result is the volume of distilled water to be added to the concentrated thiocyanate solution to make 2 c.c. of it equivalent to 1 c.c. of standard silver nitrate. This operation of adjustment is necessary because ammonium thiocyanate is rarely pure.

Calcium Oxalate.—While oxalic acid is usually stated to be a constituent of the urine, the amount should not exceed what is called *a trace*. Its combination with calcium is soluble to such an extremely small amount by the aid of the acid phosphates that anything more than a trace appears as a spontaneous deposit. Its naked-eye characters are not distinctive from those of mucus or epithelial débris. Its crystals are very minute, and call for the microscope to make out their form. It takes two different shapes, more commonly occurring as *octahedra*, which appear as bright squares with diagonal cross-lines, like envelops, and sometimes,

FIG. 102.—Calcium oxalate.

though rarely, showing as very small *dumb-bells*, or forms resembling an hour-glass (see Fig. 102).

Practical Import.—It is probable that a diet of subacid fruits and vegetables, like rhubarb or tomatoes, containing oxalates will furnish directly oxalic acid to the urine. As it is a laboratory product of oxidation changes in fats, sugars, and starches, it is easy to see why impaired digestion or retarded metabolism may be the source. Although appearing sometimes without assignable cause, it usually attends conditions to be remedied by plain diet, temperance, and outdoor life. It is frequently incidental to the gouty habit. The deposit may be transient, scanty, and unimportant, or it may be persistent and more abundant, and on these accounts serious, as indicating a disposition to the formation of a concretion of the kind known as the *mulberry calculus*. These calculi are so rough as to cause frequent bleeding in the bladder, the blood imparting a dark color.

Urea.—As it is the chief solid constituent of the urine, urea is also the most important physiologically as well as pathologically.

Its chemical formula, $CO(NH_2)_2$, shows its nitrogenous character, and presents the view held as to its nature, a carbonyl diamid (p. 193). The amount excreted daily is nearly 500 gr., or 40 gm., equal to all the other solids put together; from which it will be seen what a conspicuous rôle is played by it as a compound representing the waste of the protein or nitrogenized principles. Neutral in reaction, freely soluble in water and alcohol, though insoluble in ether, it is without color or odor, but has a bitter taste. In its chemical behavior, while it does not affect litmus, at times it is basic, and then again it may act in a compound, as acids do. From concentrated solutions it can be crystallized slowly in quadratic prisms beveled at the ends (pp. 200, 498).

If the urine be evaporated in a water-bath to the consistence of syrup and nitric acid added to it, the crystals of urea nitrate should soon form in rhombic plates or hexagonal scales. Failure to precipitate crystals under these conditions (when the urine has been evaporated one-half) would indicate deficiency in the proportion of urea in the sample.

Urea is decomposed by boiling the urine; by the action of fuming nitric acid; by free chlorin or bromin, or certain of their compounds, such as sodium hypochlorite and hypobromite:

$$\underset{\text{Urea.}}{N_2H_4CO} + \underset{\text{Sodium hypobromite.}}{3NaBrO} = 3NaBr + 2H_2O + 2N + CO_2.$$

The above equation represents the reaction of urea with sodium hypobromite. As stated, it yields sodium bromid, water, free nitrogen, and carbon dioxid. By using with the sodium hypobromite an excess of alkali, such as sodium hydroxid, as in Knop's fluid, the CO_2 is fixed in the solution as carbonate, and the only gas escaping is free nitrogen. The equation for this reaction is as follows:

$$N_2H_4CO + 3NaBrO + 2NaHO = 3NaBr + Na_2CO_3 + 4H_2O + N_2.$$

Hypobromite Method.—Different forms of apparatus have been devised to measure the free nitrogen evolved by the sodium hypobromite. The urine and the reagent are mixed and the effervescing gas is delivered at the top of a graduated cylinder open at the bottom and immersed in water serving as a gasometer. This collecting cylinder may be graduated in cubic centimeters, and in such a case the determination will be made on the basis of 1 c.c. of nitrogen evolved for 0.0027 gm. of urea. Sometimes it is graduated to read percentage, on the principle that 5 c.c. of a 2 per cent. solution of urea will yield 37.1 c.c. of nitrogen. As solutions of sodium hypobromite are unstable, in order to insure an accurate result it is best to prepare them freshly, according to the formula of Knop, and if any great interval must elapse between successive determinations, it is best to keep the reagent in two parts, each of

which is stable. *Knop's solution* is made by dissolving 100 gm. of sodium hydroxid in 250 c.c. of water. This should be kept in a separate bottle, with a stopper of rubber or of glass coated with paraffin. When the fluid is to be used, measure out 15 c.c. and mix with it 1 c.c. of bromin. Care must be observed in pouring the bromin, as the vapor is highly irritating to the eyes and air-passages.

The computation is 0.0027 of urea in the 5 c.c. of urine used for each cubic centimeter of nitrogen. Thus, if the gasometer records 7 c.c. of nitrogen, then there were $7 \times 0.0027 = 0.0189$ gm. of urea in the 5 c.c. of urine. Multiplying by 20 to get the percentage, we have 0.0378 per cent.

To calculate grains to the fluidounce, multiply the percentage by 4.55. If the apparatus be stated to have been graduated at 65° or 70° F., reasonable accuracy in results can be obtained be taking the observation in an apartment at or near that temperature. The variation of temperature indoors would then affect the volume of gas so little as to be of small moment in clinical observations. In such cases differences of barometric pressure might be ignored without seriously affecting the calculation.[1]

Hinds-Doremus Ureometer.—A form of apparatus was devised by W. H. Greene, which consisted of a single tube for the reaction and the measurement of nitrogen. The most convenient modification of Greene's idea is that known as the *Hinds-Doremus ureometer* (Fig. 103). It consists of a bulb with an upright tube (*a*) graduated so that each of the smallest divisions represents 0.001 gm. of urea in the urine used. Connected with the lower portion of the tube is a ground-glass stop-cock (*b*) which supports a smaller upright tube (*c*) graduated with a capacity of 2 c.c. Closing the cock (*b*), the bulb is filled with Knop's or Squibb's fluid diluted one-half (see p. 608), or *liquor sodæ chlorinatæ*. The opening is then closed with the thumb and the tube inverted so as to fill with the reagent. When restored to an upright position, the smaller tube (*c*) is filled to the zero mark with urine. The cock (*b*) is turned slowly, so as to admit gradually 1 c.c. of the urine to the measuring tube (*a*). Free nitrogen gas actively begins to collect at the top of the tube. If stood aside,

[1] Some gas-measuring tubes are graduated to be read at a temperature of 0° C. (32° F.) and barometric pressure of 30 in. or 760 mm.

Owing to the susceptibility of gas-volumes to variations of heat and pressure, to ensure perfect accuracy, a correction must be made according to the following formula:

$$V' = \frac{V(b-w)}{760\ (1+0.00366T)}, \text{ in which}$$

V' = volume required; V = volume observed;
b = barometer in mm.; w = tension of aqueous vapor;
T = observed temperature, Centigrade.

minute bubbles rise for some hours. But the operation may be completed in five minutes if the ureometer be shaken for that period, gently but rapidly (200 vibrations per minute). Part of the gas comes from other nitrogenous bodies than urea, such as creatinin, hippuric acid, and purins. To correct this excess in the record the number of grams of urea read off for the 1 or 2 c.c. of urine used is multiplied by Robinson's factor, 0.917. Thus, if the ureometer registered 0.015 for 1 c.c. of urine, then $0.015 \times 0.917 = 0.0137$ in 1 c.c.; Multiplied by 100, we have 1.37 per cent. of urea.

A more correct reading is obtained by submerging the whole apparatus in a pitcher or beaker until the water outside and the hypobromite inside are on a level. As the instrument is graduated experimentally at 19° C. (65° F.), no correction is usually necessary for temperature. Ordinary variations of atmospheric pressure may be ignored when the results are intended for clinical use. Immediately after using, the tube should be washed with alcohol.

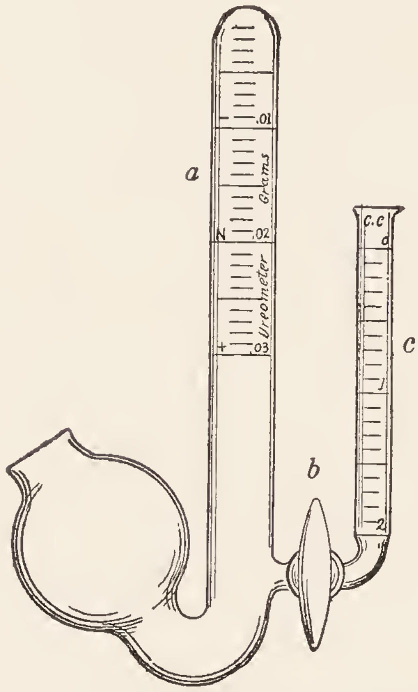


Fig. 103.—Hinds' modification of the Doremus ureometer.

Although sufficiently accurate for clinical purposes, the hypobromite process liberates only 93 per cent. of the urea nitrogen, part of the deficiency being made up from the creatinin, hippuric acid, and the purin bodies. For exact studies these other nitrogenous substances are first removed by the Morner process of precipitation, by adding a mixture of barium chlorid and hydrate to the urine along with ether and alcohol. The filtrate of ether alcohol holding urea in solution is concentrated by heat to get rid of ammonia, and is then submitted to the Kjeldahl process for determining nitrogen (p. 366).

For Pathologic Study.—It is useless to determine the urea unless the total nitrogen of intake and output are calculated for the same period. This entails so much labor that the practitioner satisfies himself with such general indications as he gets from the rapid and easy method of the Hinds-Doremus ureometer.

Use of Folin's Method.—Three c.c. of urine are placed in a 200 c.c. Erlenmeyer flask; 2 c.c. of concentrated hydrochloric acid, 20 grams of magnesium chlorid, and a small piece of paraffin are added. The flask is then connected with a long glass safety tube to condense the vapors and prevent loss of material. The contents are boiled until each drop of reflow makes a very perceptible thump; the heat is then reduced, and the boiling is continued one-half hour. Allow the contents of the flask to cool slightly and transfer the con-

tents to a liter Kjeldahl flask, washing out the original flask with about 500 c.c. of water. Add from 8 to 10 c.c. of 20 per cent. sodium hydroxid solution and distil off the ammonia into 25 c.c. of $\frac{N}{10}$ sulphuric acid. In order to be certain that all the ammonia is driven off about 350 c.c. of distillate are necessary, which amount will ordinarily pass over within one hour. Titrate back the unused sulphuric acid with $\frac{N}{10}$ sodium hydrate solution, using alizarin red as an indicator, titrating to the red point, and not to the purple. If phenolphthalein be used as an indicator, the distillate must be boiled to expel carbon dioxid. Each cubic centimeter of $\frac{N}{10}$ ammonia present equals 0.1 per cent. of urea, or 1 gm. of nitrogen found represents 2.143 gm. of urea. From this figure the amount of preformed ammonia, as well as that present in the magnesium chlorid, must be subtracted (p. 628).

In this method the principle is that at 160° C. the magnesium chlorid boils in its water of crystallization decomposing urea into NH_3 and CO_2. As HCl is present the NH_3 is fixed at once. The ammonium chlorid thus formed is decomposed by the sodium hydroxid, and the NH_3 in the distillate is caught by the standard acid solution.

Practical Import.—Urea being freely soluble never figures as a spontaneous urinary deposit. Morbid conditions causing increased tissue waste will always run up the proportion of this product. In fevers and divers inflammations the amount is increased in the early, or forming, stage and then declines with the febrile movement. In all acute diseases, as well as in phthisis, the rate of excretion rises and falls with the exacerbations of fever. In acute yellow atrophy of the liver at first it may be increased, but soon it declines notably, and in the end may disappear utterly. There is apt to be a marked lessening in the proportion when acute or chronic Bright's disease affects the eliminating powers of the kidney. Eventually this brings on the very dangerous symptoms of uremia. When urine is retained in the bladder from diseases which interfere with complete evacuation, the ready conversion of urea, which is locally innocuous, into irritating ammonium carbonate causes it to figure as a pathologic factor.

Uric Acid.—The chemical formula of uric acid, $C_5H_4N_4O_3$, shows its derivation from the nitrogenous principles of the body.

Its structural formula (p. 494) as a trioxypurin shows that it is formed through oxidation of purin groups. Much of it is changed to urea in the liver, kidneys, and muscular tissue, but some is eliminated in the urine. While it resembles urea in containing nitrogen and in its origin, it is very unlike it in other respects. The average daily quantity excreted is only 10 gr. or 0.7 gm. Taking 40,000

parts of water for its solution, it may be considered as practically insoluble in that medium, though dissolving in 1000 parts of blood-serum and freely soluble in the alkalis and solutions of the alkaline carbonates. A trace of the free acid may be discovered in normal urine, but anything more than a mere trace will be precipitated, and then it has pathologic significance. The 10 gr. eliminated daily are not free, but combined with sodium and potassium as urates, soluble at ordinary temperatures by the help of the alkaline phosphates, which prevent decomposition by the acid salts of the urine. A dense urine kept long enough to pass into the acid fermentation will throw out the uric acid along with acid sodium urate and calcium oxalate. The acid can be separated from its bases artificially by adding 10 parts of hydrochloric acid to 100 of urine. After standing forty-eight hours minute brown crystals of uric acid will fall. To collect these, and thereby obtain an approximate estimate of the amount, the supernatant urine should be decanted, the sediment washed by stirring it with 30 parts of water, and then collected by throwing them with the water upon a weighed filter. After drying the filter with its sediment in a hot-air chamber it can be weighed again, and then, allowing for the weight of the paper, the weight of the crystals can be ascertained.

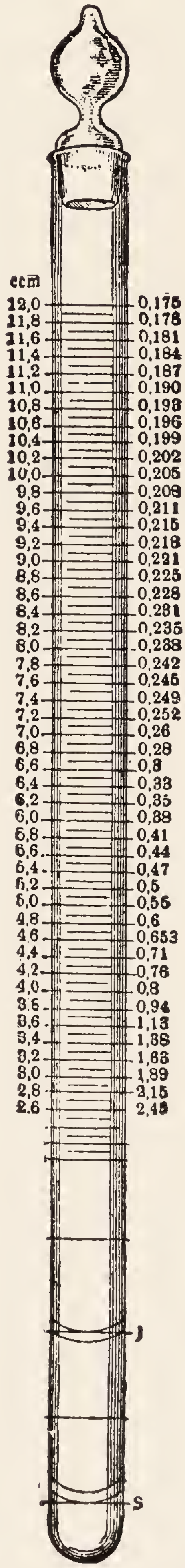


FIG. 104.—Ruhemann's uricometer.

Ruhemann's Uricometer for the Rapid Estimation of Uric Acid.—This test is based on the principle that a brown iodin solution is neutralized by a certain proportion of uric acid until the brown color vanishes completely. Its author has calculated the exact amount of iodin and potassium iodid necessary to determine the percentage of uric acid in a given amount of urine, and on that basis has constructed a graduated scale.

Fill the dry glass tube shown in diagram (Fig. 104) to the lowest mark *S* with carbon bisulphid. The lowest part of the convexity (double meniscus) has to be even with mark *S*. A solution consisting of 1.5 gr. iodin, 1.5 gr. potassium iodid, 15 gr. absolute alcohol, and 185 gr. distilled water is added as much as will fill up to the mark *J*, as

shown in the illustration. Then add the urine to the mark 2.45 (2.6 c.c.). Close the tube with the glass stopper and shake well, when the carbon bisulphid will separate of a dark copper-brown color. After adding more urine under continued shaking the carbon bisulphid will absorb all free iodin and the mixture will look like urine. Slowly adding more urine will change the yellow foam, created by shaking, into white foam. The color of the carbon bisulphid turns violet, and finally violet-pink. Should this color remain the same after the apparatus has been reversed and shaken repeatedly, add another drop of urine and keep on adding and shaking until only a slightly reddish coloration of the carbon bisulphid remains. Now shake again vigorously, and the carbon bisulphid will turn porcelain white and the urine will look like cloudy whey.

Precaution.—Stop adding urine as soon as the carbon bisulphid shows only a slightly reddish tint, because this will disappear entirely after repeated shakings. The test is finished when the indicator appears snow-white, a sign that all iodin has been neutralized by the urine.

To get rid of the remaining foam move the tube a few times slowly to a horizontal position, then open the stopper a little, to allow all liquid to settle in the tube. The proportion of uric acid is then read off at the surface of the fluid as parts per thousand.

If the upper meniscus line of the urine be between any of the 0.1 c.cm. marks, the upper number should be read. Should the urine contain less uric acid than the apparatus will in this manner indicate, add the iodin solution to the mark halfway between *S* and *J*, and read after reaction *the half-values*. If the urine show an acid reaction, it can be used at once; but if it be alkaline, it must be made acid by a drop of acetic acid. Cloudiness is of no importance. If the urine contain a considerable sediment of sodium urate, it should be well shaken. Strong colorations of the urine do not affect the action of carbon bisulphid. This test is liable to fallacies from the presence of pathologic or medicinal substances that combine with iodin. Among those that must be carefully excluded are sugar, albumin, pus, blood, bile, diacetic acid, aspirin, and antipyrin. It is fairly accurate so long as the general uric acid metabolism is low. At 0.3 gm. per day the error will not exceed 15 per cent.; above 1 gm. the limit of inaccuracy cannot be safely stated. This test is useful for rough estimations of increasing or diminishing output of uric acid such as are required in clinical medicine.

Folin and Macallum Method.—This method is more accurate, but also more difficult, requiring time, special apparatus, and practised technic, as stated in the "Jour. Biol. Chem.," Dec. 1912: The "uric acid reagent" is phosphotungstic acid prepared by boiling 100 gm. of sodium tungstate with 80 c.c. of 85 per cent. phosphoric acid and

750 c.c. of water for a couple of hours and then diluting to 1 liter. From 2 to 5 c.c. of urine (the amount depending on the specific gravity) are measured into a 100 c.c. beaker, and after adding a drop of saturated oxalic acid solution the whole is evaporated to dryness on the water-bath or over a hot iron plate, or even over a free flame. This evaporation takes only a few minutes, but it should be continued until the upper parts of the beaker are dry. To the dry, cool residue are added 10 to 15 c.c. of a mixture, consisting of 2 parts of pure, dry ether (*i. e.*, ether distilled over sodium) and 1 part of pure methyl alcohol. After standing for about five minutes, the solution is removed by careful decantation and another 10 c.c. of the alcohol-ether mixture are added to the residue, allowed to settle, and decanted. The alcohol-ether dissolves out the phenol acids and leaves the uric acid. To the washed residue in the bottom of the beaker is next added water (5 to 10 c.c.) and a drop of saturated sodium carbonate solution, and the mixture is shaken or stirred so as to secure complete solution of the uric acid. To the solution is finally added, first, 2 c.c. of the uric acid reagent and then 20 c.c. of saturated sodium carbonate solution. The resulting blue solution is transferred to a 100 c.c. measuring flask, diluted with water up to the mark, and the intensity of the color is determined by means of a Duboscq colorimeter. The standard solution for comparison is obtained by treating 1 mg. of uric acid in lithium carbonate solution with 5.10 c.c. of water, 2 c.c. of the uric acid reagent, and 20 c.c. of sodium carbonate solution, and the whole made up to 100 c.c. in a volumetric flask.

The **centrifuge method** of estimating requires that the phosphates be first separated by placing 10 c.c. of urine in the percentage tube with about 1 gm. of sodium carbonate and 1 to 2 c.c. of ammonium hydrate. The phosphate precipitate is thrown down by rotation, and the clear urine poured off into another tube. To this is added 2 c.c. of ammonium hydrate and 2 c.c. of a 5 per cent. solution of silver nitrate (to which ammonium hydrate has been added until the first precipitate clears up); and the translucent precipitate of silver urate is separated by rotation. Having poured off the clear liquid, the precipitate of silver urate is washed free of chlorid by mixing it with at least 5 c.c. of ammonium hydrate. The mixture is then well rotated until the precipitate is reduced to its least bulk. For $\frac{1}{10}$ c.c. of this precipitate the uric acid is read off as 0.001176 gm. in 10 c.c. of urine. To get percentage this product is again multiplied by 10. Thus: if the reading was 0.5, then $5 \times 0.00176 = 0.00588$ gm. in 10 c.c. or 0.0588 per cent.

Murexid Reaction.—Uric acid, free or in combination, can be identified by the murexid reaction. To obtain this the suspected substance is treated in a watch crystal or porcelain dish. After

adding a few drops of strong nitric acid, enough to dissolve, a slow heat is applied to evaporate the solution to dryness. A yellow or reddish residue is obtained. This, touched with a drop of aqua ammonia or held over the open mouth of the bottle of ammonia, should turn to a bright crimson, purple, or violet (murexid) (p. 495).

If the crystals of uric acid be examined under a microscope, they are found to be of a pointed oval form. As they fall they take up the coloring-matter of the urine, which makes them red or brownish.

When the crystals fall spontaneously they are larger, though still minute, and can be made out by the naked eye as the only brown specks of this size found in the urine. They are not unlike grains of red sand or ground cayenne pepper. Under the microscope they appear as small reddish lozenges, sometimes broken and single, sometimes united so as to form stars, rosets, or sheafs. These are all modifications of the simple rhomb or *whetstone*. (See Fig. 105 and Plate 7, Fig. 5.)

Practical Import.—Deposits of crystalline urates in the joints and kidneys are one expression of the gouty diathesis, in which there is a tendency for the nitrogenous waste to take this shape. Cases occur, not otherwise related to gout, in which the urine deposits free uric acid spontaneously. If this happens only in concentrated urine or when several hours have elapsed after micturition, and as a consequence of the acid fermentation, it may be ignored safely. The same crystals, however, seen in a sample soon after micturition should awaken the suspicion that the sediment likewise falls in the bladder or in the kidney. If persistent, these would aggregate into calculous masses. About 80 per cent. of all the urinary concretions are composed of uric acid alone or mixed with urates. The solubility of these in alkaline fluids is the basis for preventive treatment by the liberal exhibition of the alkaline bicarbonates or citrates.

Purin Bodies.—In another place (p. 495) consideration is given to the relationship held by uric acid to the other purin bodies, the xanthin bases, which are present in the urine in the proportion of 1 : 10 of uric acid. At the same place is discussed the distinction between endogenous and exogenous uric acid. We have complete control over the exogenous uric acid by regulating the diet so as to reduce the nucleins and purins to a minimum (p. 498).

Mixed Urates.—Under this title are included salts of uric acid with sodium, potassium, and perhaps ammonium, magnesium, and calcium, which in normal urine are soluble at ordinary temperatures. If, however, morning urine of ordinary acidity and density be kept in a cold room, its solvent powers are les-

sened, and it may become turbid, forming a surface film and throwing down these mixed urates as a loose pink powder. Even at common temperatures this sediment may occur if the urine be very dense and of higher acidity than usual. In such cases the urates may not in themselves be in excess, but the urine, owing to hyperacidity, becomes a poorer solvent for them. These conditions are very frequent, and hence this deposit is a very familiar one; it is sometimes known as the *lithate* or the *lateritious* or the *brick-dust deposit.* It is not at all difficult to recognize, being the only deposit which clears up when the urine is heated. Again, it is dissolved when potassium hydroxid is added to the urine. The same procedures would leave a phosphatic deposit unchanged, or even increase the turbidity. In case of doubt the murexid test (see Uric Acid) would act with the urates. (Plate 7, Fig. 1.)

Microscopically, the urates are found to be amorphous granules with a tendency to form moss-like groups, pinkish in color (Fig. 105). To distinguish them from amorphous phosphates, a drop of potassium hydroxid may be caused to flow under the cover. The urates will dissolve, but the phosphates are unaffected. (Plate 7, Fig. 4.)

Practical Import.—By referring to the conditions producing them, it will be seen that before attaching much importance to this deposit it must be ascertained if the urine has been kept in a cold place. If not, then the deposit may be one evidence of excess of acid urates due to increased waste of nitrogenous tissue, such as occurs in fever. This may be transient, as from cold, or persistent, as in chronic diseases causing hectic fever. Sometimes it is the expression of a habit of defective oxidation, or it may be assignable to a free indulgence in meats and heavy liquors. The urine can be cleared up quite easily by making it alkaline, and sometimes by merely lowering its acidity. For this the usual remedy is potassium citrate in doses of ½ to 1 dr., given in an effervescent draught. If the urates be persistently deposited while the urine is in the bladder, they tend to accrete about a nucleus, and thus gradually form a concretion.

Fig. 105.—Uric acid and mixed urates (Funke).

Ammonium Urate.—This compound of uric acid has some properties differing from those of the mixed urates referred to above. It will form as a deposit in urine made ammoniacal by putrescence, and then appears in company with the triple phosphate crystals. Under the microscope it is seen as dark-brownish spherules. Under this title some writers class a deposit made of irregular spherules with spiny projections. These have been called *hedgehog crystals.* Occasionally they look not unlike an acarus insect (Fig. 100).

Practical Import.—The dark spherules are simply incidental to ammoniacal fermentation. The spiny globes are sometimes seen in the dense, scanty, high-colored urine passed by children in febrile attacks. Concretions are very apt to be formed by them if the attacks are of frequent occurrence.

Sugar.—Sugar in anything more than a very minute amount is absent from healthy urine. Some of the urinary constituents, such as uric acid and creatinin, and the glycuronates of indol and skatol, and a number of accidental drugs, can be made to exhibit reducing powers resembling those of glucose. In normal urine this power is not marked enough to appear distinctly with the usual reduction tests when properly made, whereas in true glycosuria it is shown to a pronounced degree. It is well to remember that high-colored, acid, and dense urines contain a relatively large amount of uric acid and creatinin, and that with such samples additional care should be observed to avoid a fallacy. It is always advisable before testing for glucose to make sure of the absence of albumin.[1]

Glucose as a Reducing Agent.—The most striking tests make use of the property possessed by glucose of reducing salts of copper and bismuth to lower oxids, or even to the metallic state, when boiled with these salts and an excess of alkali (Plate 8, Figs. 1–4).

Trommer's test is made with ½ in. of urine in the test-tube, to which is added an equal amount of potassium hydroxid (liquor potassæ) and a few drops of a solution of copper sulphate. These are heated over a spirit lamp or a Bunsen's burner until boiling begins. A red or yellow precipitate of cuprous oxid denotes glucose. This is a crude and sometimes fallacious method of testing with copper sulphate. To obviate its defects it is best to make the alkaline copper solution first and bring it to the boiling-point before adding the urine. But when the alkali and the copper sulphate are mixed, an objectionable precipitate of cupric hydrate forms. The change into an insoluble hydrate can be prevented

[1] *Artificial saccharin urine* for students' practice can be made by adding to normal urine a small quantity of the ordinary syrup sold by grocers, which is mainly glucose.

by adding certain carbon compounds, such as the tartrates, glycerin, mannite, and glucose. Of these, however, glucose only has the power to abstract oxygen from the boiling copper solution, throwing down the red or yellow cuprous oxid (p. 303).

The **glycerin cupric test** may be accurately applied by mixing in the tube an inch of potassium hydroxid, a few drops of copper sulphate solution, and a drop or two of glycerin. Having heated this mixture to boiling, about 10 drops of suspected urine should be added. After waiting a few seconds, if the yellow or red precipitate does not appear, the mixture must be brought to the boiling-point again and a few drops more of urine added. This process must be repeated until the yellow or red precipitate appears or until the total contents of the tube reach 2 in. The yellow or red precipitate denotes glucose. In practice it is very convenient to have the glycerin and copper ready mixed. This is done by dissolving 28 gr. of copper sulphate in a mixture composed of $\frac{1}{2}$ fl. oz. of water and $\frac{1}{2}$ fl. oz. of pure glycerin. To make the test fluid, several drops of this are added to an inch of potassium hydroxid. *Fehling's solution* differs from the preceding in using a tartrate as the medium for making a clear alkaline copper fluid. It may be made and contained in a single bottle, but in that shape does not keep well, depositing the red oxid of copper spontaneously. It is better to have its components in two separate bottles labeled *A* and *B*, of which equal parts are to be mixed when used. To make solution *A*, mix copper sulphate 34.64 gm. and water enough to make 500 c.c. For solution *B*, mix Rochelle salt 173 gm., solution of sodium hydroxid (specific gravity 1.33) 100 c.c., and water enough to make 500 c.c. To make Fehling's solution mix equal parts of *A* and *B*.

Fehling's test is made by putting about $\frac{1}{2}$ in. of the above solution into a test-tube and diluting it with 2 in. of water. When heated to the boiling-point add a small amount of urine. If no red or yellow precipitate appears, heat to boiling again and add another instalment of the urine short of an inch in amount. Heat to boiling again and watch it as it cools; the slightest yellow or red turbidity would indicate glucose.

In all the above copper tests care should be taken that the test fluid should exceed the urine in volume, and that the contents of the tube *should not be boiled*, but merely heated to the point of boiling and then withdrawn from the flame.

Volumetric Estimation.—Having mixed in a porcelain capsule 10 c.c. of Fehling's solution and 40 c.c. of water, the mixture should be heated over wire gauze until boiling begins. While thus heating a buret may be charged with a mixture of 1 volume of urine to 9 of water. This diluted urine should be allowed to

drop slowly from the buret into the gently boiling test-fluid until the blue color of the copper solution totally disappears. Having noted the number of cubic centimeters required, if great accuracy be desired, the whole process may be repeated with fresh materials, dropping the urine very slowly as the reaction approaches its end. The solution has been standardized, so that 10 c.c. of it will be decolorized by 0.05 gm. of glucose.[1] If it be found that 7 c.c. of the dilute urine were needed, then, as the urine was diluted 1 part in 10, we read it 0.7 c.c. of urine = 0.05 gm. of glucose. Parts per hundred can be calculated by the ratio 0.7 : 0.05 :: 100 : x = 7.14. To get grains to the fluidounce, the 7.14 must be multiplied by the factor 4.55.

Purdy's Volumetric Method.—In practice the beginner finds that the Fehling's precipitate of copper suboxid obscures the color indications and errors are frequent from this difficulty. To obviate it the solution for quantitative purposes is best made with ammonia, which holds the copper salts in solution. There is no precipitate to cloud the end-point of the reaction, and the change is sharp from the blue fluid to one that is yellowish.

To make Purdy's solution, take copper sulphate 4.75 gm.; glycerin 38 c.c.; dissolve in 200 c.c. of water by heat. In another 200 c.c. of water dissolve potassium hydroxid, 23.5 gm., and mix with the copper glycerin solution. When cool, add strong ammonia water, 450 c.c., and water sufficient to make 1000 c.c. It makes a sapphire-blue solution.

Method.—Put in a capsule or beaker 35 c.c. of the above solution and 70 c.c. of water. Put in the buret the plain urine. Boil steadily and add, drop by drop, the urine until the blue liquid is colorless and transparent. For the total cubic centimeters of urine used calculate 0.02 gm. of sugar. If the quantity of urine used was 4, then

4 c.c. = 0.02
1 c.c. = 0.005
therefore, the percentage or 100 c.c. = 0.50.

If less than 4 c.c. are required, dilute the urine by adding 2 parts of water and then multiply the result by 3. The advantages found in students' work are the definite end-point, stability, rapidity, and accuracy.

A fallacy results from the fact that the normal reducing power of urine from uric acid, creatin, etc., is equivalent to about 0.5 per cent. of glucose. Hence some dense, high-colored urines may discharge the blue color after prolonged boiling, even when free from sugar. The whole titration must be done quickly, as the decolorized solution regains its blue color on standing a few minutes.

[1] The same quantity, 10 c.c., requires to reduce it, 0.067 gm. of lactose and 0.074 of maltose.

Benedict-Fehling Solution.—In this, the best modification, the reagent does not deteriorate when kept, is a much more delicate test for glucose, and is not reduced by uric acid, creatinin, chloroform, or the simple aldehyds. The rare conditions, alkaptonuria and excessive glycuronic acid excretion, cause reduction of this solution as they do of Fehling's. They are detected by persistence in reducing power after twenty-four hours' fermentation of the urine.

Benedict's qualitative solution has the following composition:

	Gm. or c.c.
Copper sulphate (pure crystallized)	17.3
Sodium or potassium citrate	173.0
Sodium carbonate (crystallized) (or one-half if dry)	200.0
Distilled water to make	1000.0

The citrate and carbonate are dissolved together (with the aid of heat) in about 700 c.c. of water. The mixture is then poured (through a filter if necessary) into a larger beaker or casserole. The copper sulphate (which should be dissolved separately in about 100 c.c. of water) is then poured slowly into the first solution, with constant stirring. The mixture is then cooled and diluted to 1 liter.

Method.—With 5 c.c. of the reagent in the test-tube only 8 or 10 drops of the urine are added. Boiled vigorously for two minutes, if glucose be present an opaque precipitate fills the solution—red, yellow, or greenish. Only on cooling would the precipitate appear if the amount be less than 0.3 per cent.

Benedict's Volumetric Estimation.—In this new and accurate method the copper is precipitated as *snow-white* cuprous sulphocyanate. The quantitative solution keeps indefinitely, and is probably more exact than any other used for glucose titration. It has the following composition:

	Gm. or c.c.
Copper sulphate (pure crystallized)	18.0
Sodium carbonate (crystallized)	200.0
Sodium or potassium citrate	200.0
Potassium sulphocyanate	125.0
Five per cent. potassium ferrocyanid solution	5.0
Distilled water to make a total volume of	1000.0

With the aid of heat dissolve the carbonate, citrate, and sulphocyanate in enough water to make about 800 c.c. of the mixture, and filter if necessary. Dissolve the copper sulphate separately in about 100 c.c. of water and pour the solution slowly into the other liquid, with constant stirring. Add the ferrocyanid solution, cool, and dilute to exactly 1 liter. Of the various constituents, the copper salt only need be weighed with exactness. Twenty-five c.c. of the reagent are reduced by 50 mg. of glucose.

Sugar estimations are conducted as follows: The urine, 10 c.c. of which should be diluted with water to 100 c.c. (unless the sugar-con-

tent is believed to be low), is poured into a 50 c.c. buret up to the zero mark. Twenty-five c.c. of the reagent are measured with a pipet into a porcelain evaporation dish (25–30 cm. in diameter), 10 to 20 gm. of crystallized sodium carbonate (or one-half the weight of the anhydrous salt) are added, together with a small quantity of powdered pumice-stone or talcum, and the mixture heated to boiling over a free flame until the carbonate has entirely dissolved. The diluted urine is now run in from the buret, rather rapidly, until a chalk-white precipitate forms and the blue color of the mixture begins to lessen perceptibly, after which the solution from the buret must be run in a few drops at a time until the disappearance of the last trace of blue color, which marks the end-point. The solution must be kept vigorously boiling throughout the entire titration. If the mixture becomes too concentrated during the process, water may be added from time to time to replace the volume lost by evaporation. The calculation of the percentage of sugar in the original sample of urine is very simple. The 25 c.c. of copper solution are reduced by exactly 50 mg. of glucose. Therefore, the volume run out of the buret to effect the reduction contained 50 mg. of the sugar. When the urine is diluted 1:10, as in the usual titration of diabetic urines, the formula for calculating the per cent. of sugar is the following:

$\frac{0.050}{X} \times 1000 =$ per cent. in original sample, wherein X is the number of cubic centimeters of the diluted urine required to reduce 25 c.c. of the copper solution.

If chloroform be used as a preservative in the urine, it must be removed by boiling a sample for a few minutes and then diluting to its original volume.

Böttger's Bismuth Test.—As albumin may interfere with this test owing to the sulphur it contains, it is desirable first to make sure that no albumin is present. If found, it can be separated by making the urine slightly acid with acetic or nitric acid, boiling, and when cool, filtering. About 1 in. of this urine (albumin-free) is put into a test-tube with 1 in. of potassium hydroxid and a pinch of bismuth subnitrate. The mixture, being boiled for *several minutes*, will turn brown, and the white bismuth salt will turn gray or black if sugar be present. A convenient shape is given to the reagent by Nylander in the following solution, which contains both the alkali and the bismuth oxid: Take bismuth subnitrate 2 parts, Rochelle salt 4 parts, and caustic soda (solution of 8 per cent.) 100 parts. Into a test-tube put 2 in. of urine and about $\frac{1}{4}$ in. of Nylander's solution. After boiling a few minutes change to a brown or black color would indicate glucose. The result with the bismuth test is not free from doubt until the fallacy due to sulphur compounds is eliminated. As they make a black

precipitate with lead salts, which are not affected by glucose, litharge can be used to detect them. If, when litharge is substituted for bismuth subnitrate in Böttger's test, a brown or black color be produced, then sulphur compounds are present, and may cause a black precipitate, making the test for glucose. Assurance can be made doubly sure by trying Fehling's test, which is free from liability to this fallacy (Plate 8, Figs. 3, 4).

Picric-acid-and-potash Test.—About 1 in. of suspected urine is mixed in a test-tube with $\frac{1}{2}$ in. of the saturated solution of picric acid and $\frac{1}{2}$ in. of liquor potassium hydroxid. On boiling this yellow mixture for one minute a slight deepening of color may occur in normal urine, owing to reduction by uric acid and kreatinin; but change to a dark mahogany-red color would denote glucose.

Safranin Test.—The reagent is safranin, 0.1 gm. per liter. It keeps well, is not affected by albumin, uric acid, or creatinin; 3 c.c. each of the reagent and of a 1 per cent. potassium hydroxid solution are mixed and 10 drops of urine added. When the tube is heated in a boiling-water bath for three minutes, glucose causes the deep red color to fade away to a yellowish fluorescence. The same reaction is given by certain other sugars.

Phenylhydrazin Test.—Use an ordinary test-tube, and to $\frac{1}{2}$ in. of dry powdered phenylhydrazin hydrochlorid add an equal volume of powdered sodium acetate and an inch and a half of urine. By gently heating to the boiling-point the sodium acetate dissolves; continue boiling for *two minutes*, and set aside for twenty minutes to permit the *glucosazone* to form. If sugar be present, the yellow deposit falls, and when examined under the microscope is seen to be chiefly sulphur-yellow needles of phenylglucosazone. Without sugar the deposit does not show needles, but scales and brownish globules. It gives a similar reaction with maltose, lactose, pentose, and glycuronic acid (Plate 3) (p. 481).

Fermentation Test.—Reducing substances other than glucose, such as are derived from various drugs administered, are sometimes present and render the observer liable to a fallacy if he depend on the reduction tests only. Glucose is the only substance yet found in the urine which in one hour will pass into the alcoholic fermentation (though lactose may ferment after a longer period), when brewers' yeast in compressed cakes is added to it and the mixture allowed to *work* in a warm place. After twenty-four hours the glucose will have disappeared, being resolved partly into carbon dioxid which escapes and partly into alcohol which remains. This breaking up of a dissolved solid into a lighter and a volatile part occasions a loss of specific gravity in the solution proportionate to the amount of the solid involved. Not only is this an excellent test for the presence of glucose, but by the *Roberts* method it is

available for quantitative estimates. This differential-density process is simple, requiring an accurate urinometer, some brewers' yeast, and a bottle of urine.

The specific gravity is carefully taken by a Mohr balance, a pyknometer, or a delicate urinometer, and recorded; then about 4 oz. of the urine are thoroughly mixed with half a cake of compressed yeast and set aside in a warm place (the kitchen) for twenty-four hours. Fermentation will prove conclusively that the urine is saccharine. When the fermentation subsides, the specific gravity is taken again and compared with the first observation. According to Roberts, each degree of density lost stands for 1 gr. of glucose to the fluidounce of urine. If percentage be desired, the product must be multiplied by 0.219. For example, if the specific gravity before fermentation was 1040 and that taken afterward was 1020, then $1040 - 1020 = 20$ gr. of glucose to the fluidounce of urine. This 20 multiplied by 0.219 gives 4.38 per cent. Sometimes the test is performed by collecting the carbon dioxid gas. To do this a test-tube must be filled with a mixture of urine and brewers' yeast, the thumb put over the mouth so that the tube may be inverted, and the opening immersed in a deep saucer containing the same mixture. The inverted tube having been securely fixed must be kept for twenty-four hours in a warm place. If glucose be present to an amount exceeding 0.1 per cent., some gas will collect at the top of the tube.

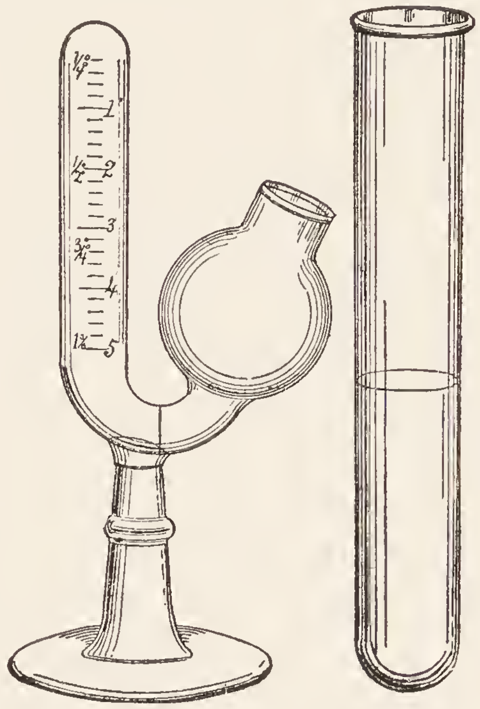


FIG. 106.—Saccharometer and mixing tube.

A more convenient and precise apparatus is *Einhorn's fermentation saccharometer.*

Method: Take one-sixteenth of a cake of compressed yeast, shake well in a test-tube with 10 c.c. of the urine; pour the mixture into the saccharometer, and by inclining the apparatus the mixture easily flows into the tube, displacing the air. Set aside in a warm room for twenty-four hours.

If the urine contain sugar, the alcoholic fermentation begins in about twenty to thirty minutes. The evolved gas gathers at the top of the tube, forcing the fluid back into the bulb.

In twenty-four hours the upper part of the graduated tube is filled with carbon dioxid gas. The level of the fluid in the tube indicates by the numbers the approximate per cent. of sugar present. If the urine contain more than 1 per cent. of sugar, it

must be diluted with water before being tested. Diabetic urines of a specific gravity of 1.018–1.022 may be diluted with an equal quantity of water and the result multiplied by 2; of 1.022–1.028, with 4 volumes of water, and the result multiplied by 5.

If we take, beside the urine to be tested, a normal one, and make the same fermentation test with it, the mixture of the normal urine with the yeast will have on the following day only a small bubble at the top of the tube. This proves the efficacy and purity of the yeast. If there be in the suspected urine only a small bubble at the top of the cylinder, then *no* sugar is present, but if there be a much larger volume of gas, then there can be no doubt that the urine contains sugar.

Polariscope Test.—When the chemical tests give a doubtful report, the polariscope should be used (p. 61).

Practical Import.—The presence of sugar in the urine, in amounts detected by ordinary tests or *glycosuria*, as it is called, proceeds from conditions regarded as essentially pathologic. In the majority of cases it is a sign of diabetes mellitus. In this disease the sugar is commonly abundant, averaging 4 per cent., but sometimes reaching the large amount of 10 per cent. or 50 gr. in the fluidounce; it persists for many months and occasions the excretion of large quantities of urine, which may amount to 2 gallons daily, pale in color and of a mellow-apple odor. With the excess of water there is an increase in other natural constituents, such as urea. The total effect of these solids and the sugar is to raise the specific gravity above the normal point. At the same time there is an obvious breaking down of the health; the patient grows emaciated, notwithstanding his voracious eating and drinking. The amount of sugar excreted and the cognate symptoms are measurably under the control of a dietetic regimen. By cutting off saccharine and amylaceous foods from the dietary, not only the proportion of sugar in the urine, but also the fluid volume, can be lessened.

It remains to be said that glycosuria is sometimes transient and slight. In some individuals, usually obese, it may appear as a consequence of excess in saccharine or amylaceous food. Temporarily, glucose, glycuronic acid, alkapton, pentose, or some other substances giving the same reduction reactions, though *not fermentable*, have been found after the administration of ether, chloroform, chloral, morphin, amyl nitrite, turpentine, salicylic acid, salol, benzoic acid, glycerin, camphor, carbolic acid, strychnin, arsenic, phosphorus, sulphonal, acetone, mercuric chlorid, phlorizin, adrenalin, urotropin, and carbon monoxid. Glycosuria may complicate various diseases of the brain and spinal cord, cirrhosis of the liver, cholera, phthisis, pneumonia, and asthma. It may appear in the last month of pregnancy and disappear soon after parturition.

Pentosuria.—Traces of pentoses ($C_5H_{10}O_5$) (p. 439) are sometimes found in the urine after ingestion of fruits, wine, and beer, and also as a result of family predisposition. The pentoses reduce Fehling's and Bottger's solutions, but not in the amounts usually found. They yield good crystals with phenylhydrazin, but they do not respond to the fermentation test and are optically inactive. Their presence is detected by *Bial's orcin test.* The reagent is made by mixing orcinol, 1 gm.; liq. ferri chloridi, 25 drops, and 500 c.c. of 30 per cent. hydrochloric acid. Of this solution 5 c.c. are boiled in a test-tube and after removal from the flame a few drops of urine are added. If a fine green color does not form, more urine is added—up to 1 c.c. Pentose causes upon cooling the green color or possibly a flaky green precipitate. This reaction is not given by normal or diabetic urine.

Practical Import.—No bad results have been noted in the few cases studied. From the mistake in diagnosing pentosuria for diabetes the patient may lose the privilege of life insurance, or be subjected to a diabetic regimen which has no effect on the pentose. Pentosuria is usually discovered by the failure of dietetic regimen to influence the reducing substance in the urine.

Glycuronic Acid.—Glucose being $CH_2OH\ (CHOH)_4\ COH$, when oxidized in the body, the alcohol group CH_2OH gives up H_2 and takes O instead, thus changing to glycuronic acid, $COOH.(CHOH)_4COH$. As this retains the COH group, it reduces Fehling's solution. It is found in the animal body and a bare trace in human urine, combined with indoxyl and phenol. Larger quantities appear in the urine after the administration of chloral, camphor, naphthol, turpentine, menthol, toluol, exalgin, morphin, etc. It forms compounds which are closely allied to the glucosids. The compounds vary according to the drug with which it is united—campho-glycuronic acid, menthol-glycuronic acid, etc. The free acid and the above glycuronates reduce the oxids of copper and bismuth in alkaline solution; hence, they may be confounded with glucose. But, unlike glucose, it does not ferment with yeast. Its presence is suspected when a sample of urine reduces Fehling's, Böttger's, or Nylander's solution, and it is levorotatory to polarized light, and *does not ferment* with yeast (p. 437).

Acetone ($CH_3.CO.CH_3$), **Diacetic Acid** ($CH_3.CO.CH_2.COOH$), **and Beta-oxybutyric Acid** ($CH_3.CHOH.CH_2.COOH$).—The last named is the mother substance derived from fat and the amino-acids of protein; oxidation converts it to diacetic acid, which by losing CO_2 changes to acetone (p. 427). A trace of acetone is usually found in diabetic urine and sometimes in healthy urine. When diabetic coma is impending, there is a large increase of acetone in the urine and diacetic acid appears, while the specific gravity, the sugar, and the urea decline. The *diacetic acid* is revealed by adding

1 or 2 drops of liquor ferri chloridi to 3 c.c. of urine. A yellowish phosphatic precipitate forms, which should be separated by filtration. If the filtrate, when treated with a few more drops of the ferric chlorid, does not yield a claret-wine color, we may safely infer the absence of the significant substance. If the wine color appear when the patient is not taking salicylic acid, antipyrin, kairin, or other phenol products, it is most likely due to diacetic acid. More elaborate control-tests can be applied to make the result conclusive, such as boiling a fresh sample, which destroys the diacetic acid and prevents the ferric chlorid reaction unless that be due to the indifferent phenol products referred to. Should the boiled sample yield no reaction, another portion acidulated with dilute sulphuric acid and extracted with ether may give the dark-red color when the extract is treated with ferric chlorid. This denotes that the diacetic acid existed in combination.[1] (Plate 8, Fig. 6.)

For **minute quantities** it is necessary to concentrate the acetone by distilling 10 c.c. from 100 c.c. and applying the tests to the distillate, or a more delicate method may be preferred. Take 50 c.c. of urine, add a few drops of sulphuric acid, and shake well with 50 c.c. of ether. The ether extracts the acid from the other urinary constituents and forms a top layer. Separate the ether and shake the extract with a small quantity of weak solution of ferric chlorid. Diacetic acid turns it red; salicylic acid turns it red violet (pp. 427 and 472).

Legal's Test for Acetone.—Mix 25 c.c. of urine with 25 c.c. of a strong, freshly made solution of sodium nitroprussid, and add a few drops of sodium hydroxid or strong ammonium hydroxid. Acetone develops a red color, and, on the addition of acetic acid, in one or three minutes becomes *darker*. Creatinin gives the red color, but it disappears on adding acetic acid.

Trommer Test.—Into about 10 c.c. of urine put about 1 gm. of sodium or potassium hydroxid solid, and without waiting for solution add 10 drops of a 10 per cent. solution of salicylaldehyd in absolute alcohol. Heated to 70° C. (158° F.), if acetone be present, a purple red color appears at the zone of contact with the sodium hydroxid. This test is distinctive of acetone and is of extraordinary delicacy.

Hart's Test for Beta-oxybutyric Acid.—To get rid of the volatile acetone and diacetic acid mix 20 c.c. of urine, 20 c.c. of water, add a few drops of acetic acid, and boil until the volume is reduced to 10 c.c. Now add water to restore the volume to 20 c.c. and divide the 20 c.c. between two test-tubes. To one tube only add 1 c.c. of hydrogen dioxid, warm gently, and allow to cool. Apply Legal's test for acetone to both tubes and stand aside for a few hours. If beta-oxybutyric

[1] For the students' practice, *ethyl aceto-acetate*, a few drops, may be added to the urine. It yields the same reaction as diacetic acid.

PLATE 8.

THE MOST IMPORTANT COLOR-REACTIONS OF THE URINE.

FIGS. 1 to 3. **Trommer's Test for Sugar.**—Potassium hydroxid and copper sulphate.

FIG. 1. Urine free from sugar does not dissolve copper sulphate and assumes a greenish-yellow color on boiling.

FIG. 2. Urine containing sugar dissolves the hydrated cupric oxid formed, with the development of a blue color, and precipitates on heating hydrated cuprous oxid in yellowish-red clouds (Fig. 3)—reduction-process.

FIG. 4. **Bismuth-test.**—Addition of Nylander's solution. On heating, metallic bismuth is precipitated in black clouds if sugar be present.

FIG. 5. **Moore's (Caramel-) Test.**—If to urine containing sugar is added one-third the quantity of potassium hydroxid and heat applied (for three minutes), a chestnut-brown color results.

FIG. 6. **Ferric-chlorid Reaction in Diabetes.**—This consists in the development of a Bordeaux-red color when diacetic acid is present in the urine, and is thought to indicate threatening diabetic coma [?].

FIG. 7. **Peptone-test.**—When albumoses, etc., are present in the urine the addition of potassium hydroxid and solution of copper sulphate in the cold is followed by the development of a violet color (*biuret reaction*).

FIG. 8. **Indican-test.**—If urine and pure hydrochloric acid be mixed in equal parts, and calcium hypochlorite in solution be added drop by drop, any indoxyl present will be oxidized into blue indigo (various intestinal disorders, fermentative processes). The mixture shaken with ether separates a blue top layer.

FIG. 9. **Test for Biliary Coloring-matter.**—On shaking with chloroform the urine from a case of jaundice the chloroform settles and assumes a yellow color (bilirubin).

FIG. 10. **Heller's Blood-test.**—On the addition of one-third potassium hydroxid and boiling, the precipitated phosphates carry the blood coloring-matter with them to the bottom in the form of red clouds.

FIG. 11. **Test for Melanin.**—In cases of melanotic sarcoma the urine treated with iron chlorid assumes a deep-black color.

FIG. 12. **Diazo-reaction.**—In cases of typhoid fever, tuberculosis, etc., the addition of a mixture of sulphanilic acid and sodium nitrite gives rise to the development of a bright-red color, apparent also in the froth on shaking.

(JAKOB.)

PLATE 8.

acid be present, it is oxidized to acetone by the hydrogen peroxid and shows a red zone in that tube. The unoxidized tube gives no reaction. The *polariscope* may be used to detect *beta-oxybutyric* acid. If the glucose be removed by fermentation with yeast, and then the clear urine tested with the polariscope, a decided rotation to the left points to this acid. Its specific rotation is 24. Then a rotation of 1° with a 2 decimeter tube would give $\frac{1° \times 100}{24 \times 2} = 2$ per cent. Slight degrees of levorotation would mean nothing, as normal urine is slightly levorotatory. Diabetic urine containing beta-oxybutyric acid registers more glucose by Fehling's test than with the polariscope, because the levorotation power of the acid neutralizes some of the dextrorotation of the glucose. To remove a possible fallacy the chance presence of the conjugate glycuronates must be considered.

Practical Import.—While traces of the "acetone bodies" have been found in fevers, indigestion, starvation, scurvy, and measles their presence in large amounts, with glucose in the urine, renders the diagnosis of diabetes certain. The gravity of the disease is proportionate to their amount in the urine. The maximum quantity may be more than 5 gm. in twenty-four hours. Death from diabetes is often preceded by a typic coma, beginning with indigestion, abdominal pain, weakness, and drowsiness. These symptoms have been attributed to an acid intoxication by the beta-oxybutyric and diacetic acids, which alter to a dangerous extent the normal alkaline salts of the blood. This condition has received the name *acidosis*. The coma attending it results from the fact that the inorganic alkalis, such as ammonium carbonate, $(NH_4)_2CO_3$, being neutralized by the acids, can no longer carry CO_2 away from the tissues where it accumulates, producing the phenomena of asphyxia (p. 424). Acetonuria is found after ether anesthesia.

Ammonia in Acidosis.—Acids are not found free in the blood. In acidosis the oxybutyric acid is neutralized by ammonia because the fixed alkalis are appropriated to other uses. Ammonia as a waste product (p. 501) is abundant and a small amount is normal in the urine. Hence toxic acids appear in urine as ammonium salts. To estimate the ammonia is to learn the amount of diacetic and oxybutyric acids. *Method:* In an evaporating dish mix 25 c.c. of fresh urine and 10 c.c. of milk of lime. A triangle made of a glass rod is placed upon this dish to support a small vessel containing 20 c.c. of $\frac{N}{4}$ sulphuric acid. Cover the whole with a bell jar greased to fit the glass plate beneath the dish and set aside for four days. If the apparatus be kept at 38° C. the time may be shortened to forty-eight hours. If instead of milk of lime we add to the urine 0.5 gm. of sodium carbonate and 10 gm. of sodium chlorid, the urea will not contribute its ammonia and the result is more accurate.

The acid now holds the ammonia set free by the lime. Colored with methyl orange as indicator, it is titrated with $\frac{N}{10}$ NaHO. The equivalent of the original 20 c.c. $\frac{N}{4}$ H_2SO_4 would be 50 c.c. of $\frac{N}{10}$ NaHO. Then every cubic centimeter of NaHO less than the 50 required to neutralize the H_2SO_4 stands for 0.0017 gm. of HN_3 in the 25 c.c. of urine used. It is known that 2 gm. of NH_3 represent 6 gm. of organic acid, 5 gm. of NH_3 = 20 gm., and 8 gm. of NH_3 = 35 gm. If the total daily output of NH_3 in diabetic urine exceeds 5 gm., then there is danger of coma from acidosis. Even in health the proportion fluctuates, but does not exceed 1 gm. This method, devised by Schloesing, is not the most accurate nor the quickest, but is the simplest and usually sufficiently accurate for clinical purposes. If greater exactness be desired, **Folin's** more complex technic may be used. For convenience, compressed air is used instead of a suction-pump as in the original method: Set up a battery of four wash bottles. In the first, place 50 c.c. of 10 per cent. sulphuric acid to catch all ammonia which may be present in the air forced through the series of bottles. In the second bottle, place 50 c.c. of 10 per cent. sodium carbonate solution to catch any acid that may be forced from the first bottle. In the third bottle, place 10 gm. of sodium chlorid, 25 c.c. of urine, and 10 c.c. of kerosene to prevent foaming in the mixture. In the last wash bottle place 50 c.c. of $\frac{N}{10}$ sulphuric acid. When the bottles are all filled, connect them, in the order given, with tight-fitting rubber tubing, and connect the bottle, containing 10 per cent. sulphuric acid with a current of compressed air; 1 dr. of dry sodium carbonate is then added to the bottle containing urine, and a steady current of air is forced through the bottles for one and one-half hours, at the end of which time the ammonia will have been driven from the urine into the $\frac{N}{10}$ acid solution.

Titrate back the excess of sulphuric acid with $\frac{N}{10}$ sodium hydroxid, using alizarin red or rosolic acid as an indicator, and calculate the amount present in the 25 c.c. of urine, each cubic centimeter of sulphuric acid used representing 0.0017 gm. of NH_3. One gm. of NH_3 is equivalent to 6.12 gm. of beta-oxybutyric acid.

Albumin.—Of the several protein substances found at times in the urine, the two of greatest pathologic import are serum-albumin and globulin. These two have certain differences, but they are both derived from the blood under like conditions and appear together in the urine. In practice it is not necessary to discriminate between them. Other protein bodies, such as mucin, nucleo-albumin, peptone, and albumose, have, however, each a significance entirely different from that of albumin, though some

of their reactions are similar. When albumin escapes into the urine it remains dissolved, as it does in the blood-serum, and can only be detected with certainty by tests which change it to an insoluble compound called a coagulum.[1] This coagulum is permanent, and not a precipitate to clear up by the action of reagents.

Boiling Test.—Should the sample be cloudy, the portion to be tested must first be freed of suspended matter by filtration. This is easily and quickly done by resting the cone of filter-paper in the mouth of a test-tube. In a few minutes enough will be collected. When the turbidity is due to urates and apparatus for filtration is not at hand, gentle heat will serve to clear up the urine, and then, by continuing the heat to the boiling-point, the cloud of coagulated albumin will appear. The congeners serum-albumin and globulin are the only proteins that coagulate in acid fluids at 70° C. (160° F.), or even at 100° C. (212° F.), the boiling-point, to which the heat is usually carried. The test is best made with about 3 in. of urine in the tube, and if the reaction be not acid, it must be made so with one drop of acetic acid. Holding the tube aslant, the flame of the alcohol lamp or Bunsen's burner should be applied to the upper half only, while the tube is slowly revolved. It is advisable to continue heating until boiling begins. If albumin be present, the heated half grows more or less cloudy, as contrasted with the unchanged lower half. Three points must be emphasized: first, if the urine have its normal acid reaction, it is not necessary to add acetic acid; second, even when it is neutral or alkaline, only one drop of the acid should be used, lest the albumin should be converted into acid-albumin, which is not coagulated by heat; and, third, phosphates are sometimes precipitated by boiling off the dissolved CO_2 from a slightly acid specimen, but this precipitate clears up on cooling or on the addition of acid. If the white clouds appear in the boiling half, *the test must be completed by adding a few drops of nitric acid* while the urine is hot, but without further boiling; the albumin coagulum persists while the precipitated phosphates dissolve. When there is suppression of urine, the amount obtainable may be but a few drops, which is not enough for a satisfactory result by boiling the urine. A distinctive result can be had by boiling some water in a test-tube, acidulating, if necessary, and letting a drop or two of urine fall into and mix with the hot water. A white cloud forms if albumin be present.

[1] *Artificial albuminous urine* for students' practice may be easily made by putting the white of one egg in a bottle containing 3 fl. oz (or 100 c.c.) of a 2 per cent. aqueous solution of sodium chlorid, then shaking well and filtering. The filtered liquid can be kept indefinitely by adding 1 fl. dr. (or 4 c.c.) of chloroform. To make a sample closely resembling pathologic urine, add 10 c.c. of this liquid to 100 c.c. of normal urine.

This test is available for making an estimate of the proportion of albumin. If the entire contents of the tube be boiled for a few minutes, and then set aside for twenty-four hours, the flakes of albumin will fall, so as to make a layer the volume of which can be stated as compared with the total depth of urine in the tube; thus, "the sample had $\frac{1}{10}$ or $\frac{1}{5}$ moist albuminous layer." It will be seen that this does not mean that the urine contains $\frac{1}{10}$ or $\frac{1}{5}$ part by weight of albumin.

Nitric-acid Test.—*Heller's Method.*—If the urine be turbid, it must be made clear by pouring it through a cone of filter-paper set in the mouth of a test-tube. Having about 2 in. of clear urine, the tube should be inclined and nitric acid allowed to trickle down the glass, so as to form a bottom layer of about $\frac{1}{2}$ in. in depth. If the acid be introduced at the bottom by means of a pipet, a more distinct line of separation will be secured. After five or ten minutes, if appearances be doubtful, the tube should be held so that the light falls on it in such a way as to show up any haziness that may have formed. A more or less wide and distinct white belt at the line of contact of acid and urine indicates albumin. While this test used cold is not quite so sensitive as that by boiling, there are very few cases of serious albuminuria that cannot be detected by it. By keeping the acid and the urine separate, except at the line of contact, we ensure that at some point there will be just the amount of acid needed to coagulate the albumin. A reddish zone is often formed by the oxidation of normal urorosein. This method keeps the upper part of the urine unchanged, so as to be a standard for comparison. There are cases where the reaction is so questionable as to make this standard of decided value. Occasionally a dense urine so treated will throw out a cloud of urates $\frac{1}{2}$ in. nearer the surface, but not at the line of contact, Sometimes a faint band of precipitated proteins other than albumin appears about one centimeter above the line of contact. All the precipitates except albumin clear up when heat is applied. *In all cases it is best to use both heat and nitric acid.*

A quick and handy method, useful when the amount of urine is small or when there are many examinations to be made, as in hospitals or dispensaries, is to dip a pipet of $\frac{1}{4}$ in. caliber into the urine, taking up about 1 in., and then dipping the same into nitric acid 2 in. deep, relaxing the finger pressure so as to admit the acid. The finger is pressed down firmly again, the pipet lifted from the acid, and held so that a good light falls on the contents. If no change occurs, we may infer that albumin is absent. If albumin be present, within one minute a sharp white ring is formed at the contact line. Albumose and urates form a white cloud with cold nitric acid when weakened by dilution, but higher up the

tube than the line of contact with nitric acid. To make the albumin ring more positive it is desirable to apply the boiling test in addition to another acidulated portion in a test-tube.

Where only a few drops of urine are to be had the following delicate and easy method is useful: Lay a glass slide on a black surface and on it place, close together, a drop each of the urine to be tested and strong nitric acid. The drops soon join, and if albumin is present a characteristic film is formed, gradually producing a milky veil over the drop.

Picric-acid Test.—The reagent is a saturated solution made by dissolving 6 gr. of recrystallized picric acid in 1 fl. oz. of hot water, and after standing for a time decanting the clear fluid. The urine must first be free from turbidity: if necessary for this, it may be dropped through a cone of filter-paper into the test-tube until about 3 in. collect. The picric acid is then permitted to flow down the side of the tube held slanting to prevent the two fluids mixing. The yellow reagent remains on top, and if albumin be present, a more or less cloudy zone will *immediately* form in the urine as far as the picric acid diffuses downward. If the upper part of the turbid zone be heated to the boiling-point, haziness due to albumin will increase, and if the tube be set aside will subside as a compact stratum resting on the unchanged column of urine below.

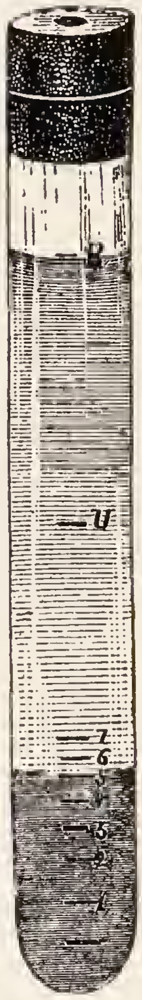


FIG. 107.—Esbach's albuminometer.

Beside albumin, the acid urates and several occasional constituents, such as mucin, albumose, peptone, semen, and the alkaloids, will yield an opalescence to picric acid. But the albumin and semen cloud is peculiar in that it persists after heating. This is a very delicate test; indeed, it sometimes reveals albumin in amounts so small as not to have significance for the practitioner. The same reaction is employed in estimating the weight of albumin by *Esbach's albuminometer*. This is a test-tube of strong glass graduated in the manner shown in Fig. 107.

The test solution is prepared by dissolving 10 parts of picric and 20 of citric acid in 900 of boiling distilled water. After cooling, a sufficient quantity of water is added to make a total of 1000 parts. The object of the citric acid is to ensure that the liquid shall overcome any possible alkalinity in the urine. The graduated tube is filled with clear urine up to the mark *U*, and then the reagent up to *R*. It is then closed with a stopper, and the

two liquids are thoroughly mixed in such a manner as to avoid shaking by slowly reversing the tube about ten times. Quick agitation might make air-bubbles that cause the precipitate to float. These must be removed with a pipet. After standing upright for twenty-four hours, a dense and well-defined coagulum of albumin falls. The height of this sediment, read off on the etched scale, will indicate the weight of dried albumin in parts per thousand of urine (grams per liter). While this process yields results which within a certain range are fairly accurate (an error of one-tenth to two-tenths of albumin), it is far more convenient than the tedious and difficult, though more accurate, method of separating the albumin by heat and acid and, after filtration, weighing the dried precipitate. Esbach's process will not give correct statements of amounts less than 0.5 parts per 1000. When the proportion of albumin is very high—that is, when the coagulum stands above 4 on the scale—it is best to dilute the urine with 1 or 2 volumes of water, and after testing multiply the result by 2 or 3, according to the degree of dilution.

A much more accurate result is given by Esbach's albuminometer, if instead of picric acid we use *Tsuchiya's* reagent. This consists of phosphotungstic acid, 1.5 gm.; concentrated hydrochloric acid, 5 c.c.; alcohol of 95 per cent., q. s. ad 100 c.c. The precipitate settles quickly and evenly without floating particles. Allowance being made for the faint precipitate yielded by normal urine, the test is valuable for comparison.

In addition to the time-honored tests already given, which have the confidence of the profession and the sanction of much usage, there remain to be described several others of great sensitiveness, but not sufficiently discriminating to be our sole reliance.

Tanret's potassiomercuric iodid reagent is composed of mercury bichlorid 1.35 gr., potassium iodid 3.32 gr., acetic acid 20 c.c., distilled water enough to make 1000 c.c. By the contact method it shows a white belt with albumin, but also with other proteins whose presence may not be at all significant. The same objection can be made to the solutions of *sodium tungstate*, of *metaphosphoric acid*, and the more complex *acetic-ferrocyanid* test. The last named is of extraordinary delicacy. It is applied by first making the urine decidedly acid with acetic acid, and then adding a few drops of recently prepared solution of potassium ferrocyanid. It precipitates albumin, but also albumose and peptone.

Spriegler's Mercuric Chlorid Test Modified.—To 5 c.c. of urine add a few drops of a reagent containing bichloride of mercury 2 gm., citric acid 49 gm., sodium chlorid 4 gm., and water 100 c.c. A white cloud at the junction denotes the presence of albumen. This is too

delicate a test as it detects 1 part of albumin to 350,000 of urine, an amount present in some cases of normal urine. It may be valuable as confirmatory of Heller's test when the reaction is faint.

Goodman's Estimation Method.—This has the advantages over Esbach's of requiring about 0.5 c.c. of urine or less and yielding a fairly accurate result in less than a minute. It is most conveniently performed in Harrower's albuminometer (Fig. 108).

Fig. 108.—Harrower's albuminometer.

Fill the tube to the mark R with 5 c.c. of *Tsuchiya's* reagent (p. 632). Having previously diluted the urine (1 in 10 is best), add the dilution drop by drop, shaking between each addition, until a faint white cloud appears at the end-point of the reaction. The level of the fluid in the tube is carefully noted. This corresponds to the amount of diluted urine that contains $\frac{1}{10}$ mg. (0.0001 gm.) of albumin. Example: 08 c.c. of diluted urine produces the reaction and is, therefore, the equivalent of .0001 gm. albumin. Then .08 c.c. *undiluted* urine equals .0001 gm.; 8 c.c. equals .01 gm., and 800 c.c. equals 1 gm. of albumin. The percentage is 800 : 1 :: 100 : per cent., or 0.125 per cent. The amount of albumin excreted in twenty-four hours is found by multiplying the percentage by the amount of urine passed and dividing by 100.

The following table will save some calculation:

C.c. of Urine reacting.	Percentage; or grammes of albumin per 100 c.c.				
	Dil. 1 in 30.	Dil. 1 in 20.	Dil. 1 in 10.	Dil. 1 in 5.	Dil. 1 in 3.
3	.100	.066	.033	.015	.01
2.8	.105	.07	.035	.017	.010
2.6	.115	.075	.038	.019	.011
2.4	.125	.082	.041	.020	.012
2.2	.135	.09	.015	.022	.013
2	.150	1	.05	.025	.015
1.8	.165	.11	.055	.027	.016
1.6	.187	.125	.062	.031	.018
1.4	.214	.142	.071	.035	.021
1.2	.25	.166	.083	.041	.025
1	.3	.2	.1	.05	.03
.8	.375	.25	.125	.062	.037
.6	.50	.33	166	.083	.05
.4	.75	.50	.25	.125	.075
.2	1.5	1	.5	.25	.15
.1	3	2	1	.5	.3

The reading must be taken *promptly* lest a fallacy be encountered. On standing a cloud may appear from precipitation of uric acid, creatinin, peptones, and albumose when present in large amount.

Purdy's Quantitative Method for Albumin (*Centrifugal*).—The centrifuge estimation by volume is performed by putting into the

percentage tube 10 c.c. of urine. To this is added 2 c.c. of 50 per cent. dilution of acetic acid and 3 c.c. of a freshly made 10 per cent. solution of potassium ferrocyanid. After shaking the mixture and standing aside ten minutes it is rotated for three minutes at 1500 revolutions per minute. For every $\frac{1}{10}$ c.c. of precipitate calculate 1 per cent. by volume of albumin layer. From this it is easy to find the percentage of dried albumin or grains per fluidounce by consulting the following table:

Purdy's Table for Estimating Albumin.

This table shows the relation between the volumetric and gravimetric percentage of albumin obtained by means of the centrifuge with radius of 6¾ in.; rate of speed, 1500 revolutions per minute; time, 3 minutes.

Volumetric percentage by centrifuge.	Percentage by weight of dry albumin.	Grains per fluidounce—dry albumin.	Volumetric percentage by centrifuge.	Percentage by weight of dry albumin.	Grains per fluidounce—dry albumin.	Volumetric percentage by centrifuge.	Percentage by weight—of dry albumin.	Grains per fluidounce dry albumin.
¼	0.005	0.025	13½	0.281	1.35	31½	0.656	3.15
½	0.01	0.05	14	0.292	1.4	32	0.667	3.2
¾	0.016	0.075	14½	0.302	1.45	32½	0.677	3.25
1	0.021	0.1	15	0.313	1.5	33	0.687	3.3
1¼	0.026	0.125	15½	0.323	1.55	33½	0.698	3.35
1½	0.031	0.15	16	0.333	1.6	34	0.708	3.4
1¾	0.036	0.175	16½	0.344	1.65	34½	0.719	3.45
2	0.042	0.2	17	0.354	1.7	35	0.729	3.5
2¼	0.047	0.225	17½	0.365	1.75	35½	0.74	3.55
2½	0.052	0.25	18	0.375	1.8	36	0.75	3.6
2¾	0.057	0.275	18½	0.385	1.85	36½	0.76	3.65
3	0.063	0.3	19	0.396	1.9	37	0.771	3.7
3¼	0.068	0.325	19½	0.406	1.95	37½	0.781	3.75
3½	6.073	0.35	20	0.417	2.0	38	0.792	3.8
3¾	0.078	0.375	20½	0.427	2.05	38½	0.801	3.85
4	0.083	0.4	21	0.438	2.1	39	0.813	3.9
4¼	0.089	0.425	21½	0.448	2.15	39½	0.823	3.95
4½	0.094	0.450	22	0.458	2.2	40	0.833	4.0
4¾	0.099	0.475	22½	0.469	2.25	40½	0.844	4.05
5	0.104	0.5	23	0.479	2.3	41	0.854	4.1
5½	0.111	0.55	23½	0.49	2.35	41½	0.865	4.15
6	0.125	0.6	24	0.5	2.4	42	0.875	4.2
6½	0.135	0.65	24½	0.51	2.45	42½	0.885	4.25
7	0.146	0.7	25	0.521	2.5	43	0.896	4.3
7½	0.156	0.75	25½	0.531	2.55	43½	0.906	4.35
8	0.167	0.8	26	0.542	2.6	44	0.917	4.4
8½	0.177	0.85	26½	0.552	2.65	44½	0.927	4.45
9	0.187	0.9	27	0.563	2.7	45	0.938	4.5
9½	0.198	0.95	27½	0.573	2.75	45½	0.948	4.55
10	0.208	1.0	28	0.583	2.8	46	0.958	4.6
10½	0.219	1.05	28½	0.594	2.85	46½	0.969	4.65
11	0.229	1.1	29	0.604	2.9	47	0.979	4.7
11½	0.24	1.15	29½	0.615	2.95	47½	0.99	4.75
12	0.25	1.2	30	0.625	3.0	48	1.0	4.8
12½	0.26	1.25	30½	0.635	3.05			
13	0.271	1.3	31	0.646	3.1			

A recently introduced test is that by *trichloracetic acid.* It is best used as a solution (specific gravity, 1.147) after the *contact method.* A white clot forms next to the reagent when albumin or albumose is present; boiling will dissipate any cloud not albuminous.

For *salicylsulphonic acid* as a test see Albumose (p. 636).

Practical Import.—Except in certain rare cases, such as the cyclic albuminuria of adolescents and in younger children, albumin is an indication of a serious disturbance in the function of the kidney. In the early hours a trace of albumin is usually present in young children and can sometimes be found in the urine of young men otherwise in apparent health. It is probable that even in these persons there is an overtaxation or alteration in the kidney, removable by time or medication. In small amounts it is often seen at certain stages of severe specific fevers and blood-poisonings, and just after epileptic seizures. In 60 per cent. of pregnant women a trace of albumin appears some time after the fifth month. This is incidental to the pressure of the gravid womb on the renal circulation. With few exceptions, the urine becomes normal soon after delivery of the child. Poisoning by lead, arsenic, and some other metals may occasion it. In every such case the question arises: Can the albuminuria be regarded as a sign of Bright's disease of the kidneys? The answer will be affirmative if the symptom prove persistent and the layer produced by the boiling test should equal one-half of the column of urine in the tube. For proof positive we must examine the sediment with the microscope for tube-casts.

The general condition must be considered, and would be regarded as highly confirmatory if characterized by anemia, cardiac hypertrophy, or dropsy. With these even a mere trace of albumin must be held to be of very grave import. Reactions of albumin with blood may be due simply to the hemorrhage, which may come from any part of the genito-urinary tract. When found with abundance of leukocytes, it may be due to the fluid of pus, and have no other significance.

Mucin (*Nucleo-albumin*).—This is a constituent of mucus which is coagulated by the organic acids—acetic, citric, picric, and trichloracetic. If mucus be present without serum albumin the urine gives, when floated on a syrupy solution of citric acid, a nebulous zone in one or two minutes. With nitric acid such urine gives no ring or cloud at the zone of contact, but a slight turbidity considerably above the acid surface. When albumin is present without mucus, no precipitate zone is formed with citric acid. That obtained with nitric acid is sharply defined and at the point of junction of the two liquids. When both albumin and mucus are present, a reaction will be obtained with both syrupy citric acid and with nitric acid. A second nebulous ring of precipitated mucus is formed above the sharply marked white

belt of albumin at the zone of contact. To discriminate, the urine must be boiled, when all clouds disappear except the one made by serum albumin.

Albumosuria.[1]—Proteoses or albumoses belong to the family of proteins, sometimes found in the urine. They appear in small amounts in various infectious diseases, and are often referable to resorption of disintegrated pus. While soluble in dilute salt solution, they are precipitated when the solution is saturated with ammonium sulphate. Heat does not coagulate them.

Tests.—To get significant amounts it is often necessary to evaporate the urine on a water-bath to less than half its volume. Into a large test-tube put 2 or 3 in. of urine with an equal volume of saturated solution of common salt, and about ½ in. of acetic acid. A precipitate forms if albumose be present, the urine clearing up on boiling and the precipitate reappearing on cooling. If it does not clear up on boiling, then other proteins are present and must be filtered off while hot. The return of the cloud as the hot filtrate cools signifies albumose.

If the hot filtrate be carefully poured down an inclined test-tube so as to form a layer with 1 in. of Fehling's solution, a rose-pink halo (*biuret reaction*) will appear at the line of contact (Pl. 8).

Salicylsulphonic-acid Test.—A convenient and sensitive reagent for distinguishing albumin and nucleoproteins from albumose is made by treating salicylic acid with sulphuric acid and crystallizing by evaporation. The crystals of salicylsulphonic acid may be safely carried about in the pocket, or, better still, a bottle of saturated solution in water may be used.

METHOD.—Two test-tubes are half filled with urine, and to each is added 1 c.c. of the solution. Shake both tubes well. If a cloudiness appear, we know that some form of albumin or albumose is present. Reserving one tube as a standard, the other is heated and then compared with the standard to see if heat have cleared up the cloud. If due to primary albumoses, it clears under heat, to reappear on cooling. If due to serum-albumin or nucleo-albumin, the cloud persists, unchanged by temperature.

This test acts in acid and alkaline urines equally well, and does not precipitate phosphates, urates, uric acid, bile, alkaloids, or drugs. In delicacy as a test for albumin it stands between Heller's cold nitric-acid and the boiling tests. Its delicacy may be counted as an objection, for quantities of albumin too small to be of pathologic importance may be shown. The most serious objection is the readiness with which *nucleoproteins* are precipitated, as at present we have no means of readily distinguishing this precipitate

[1] *Artificial albumose urine* for students' use can be made by dissolving in the urine some Witte's dry peptone.

from that caused by albumin. The best check on these two fallacies is obtained by the use of Heller's cold nitric-acid test in doubtful cases. The secondary ring higher up than the line of contact of acid and urine, given with *nucleoproteins* by this test, is readily recognizable. By diluting the urine one-half, the doubt as to the significance of the amount of albumin is set at rest. If the albumin reaction is obtained with the dilute urine, the amount is of pathologic importance.

Practical Import.—When active suppuration is going on anywhere in the body and inflammatory effusions are breaking down, albumose is a product of autolysis of the pathologic tissue. It enters the systemic circulation, and is eliminated by the kidney. It may thus help to prove the existence of concealed internal suppuration. According to the cause, it has been divided into four classes—pyogenic, inorganic, enterogenic, and puerperal.

The **Bence-Jones protein** is a rare urinary constituent closely related to the water-soluble globulin of the blood, and is recognized by the following tests: At a temperature of 60° C. (140° F.) it forms a gelatinous coagulum; at 80° C. (176° F.) it clears, and at 100° C. (212° F.) it is nearly all dissolved.

Nitric acid makes a dense precipitate which disappears when warmed and returns on cooling.

Acetic acid, up to 30 per cent., has no effect, but at 50 per cent. a jelly forms in five minutes which liquefies on warming. Salicylsulphonic acid causes a copious precipitate which dissolves when heated, to reappear on cooling.

Practical Import.—This protein appears in the urine in advance of myeloma and kindred diseases of the bone and marrow. It is always of grave significance.

Peptonuria Biuret Test.—Acidify 500 c.c. of urine with acetic acid and boil to remove the albumin. Filter this and add 5 c.c. of hydrochloric acid and then precipitate the albumoses by the addition of 3 c.c. of a 10 per cent. phosphotungstic acid. Heat the mixture gently until the precipitation is completed. Centrifugate or allow this to settle, pour off the supernatant fluid, and wash the sediment two or three times with distilled water. Again heat the sediment, and add a drop at a time a solution of 30 per cent. ammonia. If it now appears blue, continue adding the ammonia until it becomes colorless. After cooling, place some in a test-tube and add 1 drop of a 1 per cent. solution of copper sulphate; if peptone be present, an amethyst-red color will appear.

Hematuria.—Blood imparts to urine the reaction of albumin contained in serum and a red or brown color due to the corpuscles. The change of color and the albumin reactions may be found in

hemoglobinuria, a condition in which the distinct corpuscles are not found, the color principle being diffused.[1]

The characteristic feature of true hematuria is the red blood-corpuscle. These biconcave bodies will preserve their peculiar form for several days if the urine containing them is of ordinary density and acidity. In a very dense urine they lose their smooth outline and become crenated. In a dilute medium they swell up to a spheric shape and grow pale. In the ammoniacal urine which usually attends cystitis they are apt to shrivel and be deformed.

Practical Import.—Hematuria is a symptom of hemorrhage from some part of the genito-urinary tract. When the bleeding is at the kidney, the blood is usually well mixed with the urine, giving it a smoky-red appearance, and when the sediment falls, bloody renal tube-casts can be found with the microscope. It denotes active local mischief, or may be symptomatic of severe fevers or neurotic or toxic or vicarious to menstruation and hemorrhoids. Blood from the ureter is apt, before evacuation, to form clots which are molded in that tube in the shape of curved cylinders, looking to the naked eye like small worms. They have been mistaken for parasitic entozoa. The microscope shows them to be a compact mass of red corpuscles. They may be due to local disease or injury, or incidental to the passing of a renal calculus. Blood from the bladder is usually abundant and gives to the urine a bright red color, with shreddy clots visible to the naked eye. It is accompanied by vesical symptoms, such as pain in the suprapubic region and perineum, with frequent micturition and strangury. Blood from the urethra occurs in the course of gonorrhea, and reveals its source by local symptoms and by escaping at the meatus in the intervals of micturition (Plate 7, Fig. 3).

Heller's test for blood-pigment is made by adding one third potassium hydroxid and boiling until flocculi of phosphates form. As they fall they carry with them the blood-pigment and become brown or red-yellow. Having collected the precipitate on a filter, it dissolves in acetic acid with a red color, which gradually fades on exposure. It is an easy and satisfactory test (Plate 8, Fig. 10).

Benzidin Test.—A much more sensitive test for blood-pigment is made by treating 10 c.c. of urine with 1 c.c. of glacial acetic acid. To this mixture a third volume of ether is added, well shaken and set aside. The supernatant layer of ether separates more quickly if 5 to 10 drops of alcohol be shaken with the mixture. With a pipet the ether is transferred to another test-tube containing the

[1] *Artificial bloody urine* can be conveniently prepared from fresh blood or from blood preserved in glycerin or from scales of dried blood kept on hand. When needed, the scales are ground up in a mortar with water and filtered. The filtrate may be added to normal urine.

benzidin reagent, which has previously been made by mixing 0.5 c.c. of a freshly prepared solution of a little benzidin in 2 c.c. of glacial acetic acid with 2 or 3 c.c. of hydrogen dioxid.

If blood is present, the reagent turns green or blue in two minutes; after five minutes it changes to a dirty purple. The test is both accurate and reliable to the extent of a negative result, excluding the possibility of blood. As there are a number of substances which give the same reaction, if a positive response be obtained, this must be confirmed by the guaiac and the hemin tests (p. 536).

Meyer Test for Hemoglobin.—In making the reagent, zinc reduces the red phthalein to a colorless phthalin. In testing, the hemoglobin reverses the operation by carrying oxygen from the hydrogen dioxid. The *reagent* is 2 gm. of phenolphthalein and 20 gm. of potassium hydroxid dissolved in 100 c.c. of distilled water, to which are added 10 gm. of pulverized zinc. The mixture is boiled for four minutes, shaking the vessel; the fluid, red at first, rapidly loses its tint. As soon as it is decolorized it is filtered; thus prepared it will keep for months. The *test* is made with 2 c.c. of urine mixed with 1 c.c. of the reagent, well shaken; then 3 or 4 drops of hydrogen dioxid solution are added. If blood be present the fluid turns bright red, the rapidity of the change and intensity of the tint proportionate to the amount of blood present, the lowest limit of delicacy being 1 to 100,000. The reaction is not influenced by pus, albumin, pigments, sugar, uric acid or urates, acetone, indican, etc., nor by the ordinary drugs.

Hemoglobinuria.—In certain *dissolved states of the blood* the coloring-matter is set free from the disintegrated corpuscles and eliminated by the kidneys. It imparts to the urine a dark-brown color. The albumin reaction is obtained by all the tests for that substance. However, the coagulum formed is not white, but red or brownish. To distinguish this condition from hematuria the microscope is necessary.

In hematuria we not only have the color and the albumin reaction, but also the red corpuscles. The latter are not found in hemoglobinuria. With the spectroscope the dark bands of reduced blood-pigment can be identified by the special means employed with that instrument (Plate 4, Fig. 1, f–h). Almen's test by overlaying with urine a mixture of tincture of guaiac and a solution of hydrogen peroxid (or old ozonized oil of turpentine) gives a characteristic blue color (pp. 536 and 572). When properly performed Almin's guaiac test is so delicate that with a negative result other tests are superfluous. The urine must be slightly acid. While pus also yields the blue color with tincture guaiac, it does so without the addition of hydrogen peroxid and the blue disappears when heated, whereas the blue color caused by blood persists even at the boiling-point.

Practical Import.—Hemoglobinuria occurs in various blood diseases, microbic and otherwise, such as typhus, purpura, and pyemia. Sometimes it is the result of the toxic action of hydrogen arsenid, phosphorus, carbolic acid, chloral, or potassium chlorate. Certain individuals suffer from a periodic form, often attributable to cold or malaria, and sometimes of doubtful origin.

Bile.—In conditions causing jaundice we can always find bile-pigment in the urine, but the biliary acids are seldom present in amounts great enough to give the lake-colored reaction with the well-known Pettenkofer's test by cane-sugar and sulphuric acid (Plate 8, Fig. 9).

Oliver's test for biliary acids, peptone solution, is very sensitive, but gives results so uncertain as not to merit detailed description in a practical study of the urine as brief as this is required to be. On the other hand, the bile-pigment can be detected in the urine of icterus even earlier than it will show itself on the conjunctiva. When notably present, it gives tints varying from bright sulphur yellow to olive green.

Gmelin's test for biliary pigment is very sensitive and easily performed. A few drops of the suspected urine are poured in a white plate, and near them a small amount of yellow nitric acid (containing lower oxids of nitrogen). Having caused the two fluids to touch edges, bile-pigments will change at the line of contact into modified pigments. There will be a play of colors in regular order—green, blue, violet, red, and yellow. Green and red dominate, and will persist after the others fade. The same test can be applied in a tube by overlaying the nitric acid with the biliary urine. A delicate method is to filter 5 c.c. or more through a small paper and afterward put a drop of concentrated nitric acid into the cone. The white paper makes a good background for the changing colors.

Practical Import.—A trace of bile found will help to diagnose hepatic troubles when the icterode hue elsewhere is doubtful.

Pyuria.—It has been stated above that sometimes the albuminuria may be due to pus, the fluid of which is albuminous. The distinctive elements of pus are the numerous leukocytes. These, under the microscope, can be recognized by their resemblance to the white blood-cells. They are spheric, granular, and opaque, but on the addition of acetic acid lose their opacity and show at the center one, two, or three nuclei. One cannot be sure from the form whether the leukocyte is derived from mucus or from pus. With the former comparatively few are to be found, with the latter a great number. Mucus can be further distinguished from the pus from the fact that the proteid mucin will not become hazy with heat and nitric acid, while the albumin of *liquor puris* coagulates

like serum-albumin. Again, if the suspected sediment be separated by decanting the upper part of the urine, and then into the deposit a piece of caustic potash is stirred, if the deposit be pus, it becomes tough and gelatinous; if mucus, thin and flaky (Plate 7, Fig. 2).

Practical Import.—If pyuria, the albumin reaction raises the question as to whether in addition to pus there is serum-albumin of renal origin. We are helped to a conclusion by the fact that the albumin in pyuria is usually scanty, and a large amount would therefore be considered as over and above that due to pus. If tube-casts are found with the microscope, then renal mischief can be assumed. A sudden irruption of pus would most likely be due to the evacuation of an abscess into the genito-urinary passages. Persistent pyuria points to chronic catarrhal inflammation, the site of which can be determined by local symptoms.

Chyluria.—Chyle is rarely found in the urine. At first sight of a sample containing it one would suppose that milk had been added to it. It may happen that the amount of chyle present is so large that the fat particles rise like the cream on milk, and the fibrin of the chyle may form a spontaneous clot, resembling *blanc-mange.* As the chyle contains serum-albumin, it would respond to the tests for that substance. To make out the fatty character of the suspended part, a portion of the urine should be agitated with ether and potassium hydroxid, which dissolves the envelopes and melts the fat particles together as a surface layer, leaving the urine clear beneath. The microscopic character is much like that of milk—that is, it contains myriads of small, bright, round particles which dissolve in ether. To eliminate the chance of deception from milk, the patient can be required to urinate in the presence of a witness.

Practical Import.—This symptom generally appears in those who have lived in the tropics, where it is not very uncommon. It denotes a lymphatic connection with the urinary passages, and not infrequently is associated pathologically with the presence of *Filaria sanguinis hominis.*

Epithelium.—Ordinarily the urine is clear, but even in health it occasionally shows a faint cloud called the *nubecula,* which the microscope reveals to be made of epithelial débris. In some persons a small amount of the waste material of cells from the mucous lining of the bladder and other parts of the urinary tract may occur, and have no significance. A large amount with mucus, or still more with pus, would indicate catarrh of some portion of the urinary tract. Practically, the main point to be determined is as to whether the cells are from the kidney or not.

Renal epithelium is spheric, granular, and nucleated, with an indistinct cell wall. The coexistence of casts of the uriniferous

tubules would corroborate their testimony as to the existence of renal desquamation. Cells from extrarenal parts are distinct,

FIG. 109.—Epithelium from the urine: *a*, *b*, Epithelium from the bladder, from the pelvis of the kidney; *c*, caudate epithelium (pelvis of the kidney?); *d*, renal epithelium partly changed into fat (Vierordt). *Greatly magnified.*

nucleated, and flattened, being oval, spindle-shaped, cylindric, or tessellated, according to site. Cylindric or caudate cells may be derived from the pelvis of the kidney, from the prostate gland, from Cowper's gland, from the urethra, or from some parts of the bladder. Bladder epithelium is usually flat and irregularly oval; sometimes desquamation occurs in patches of cells joined at their edges. In the urine

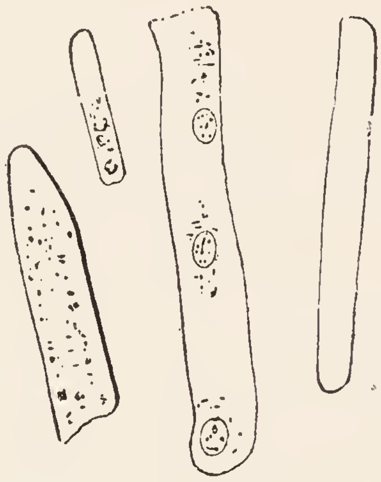


FIG. 110.—Hyaline casts (narrow and tolerably broad ones). *Greatly magnified.*

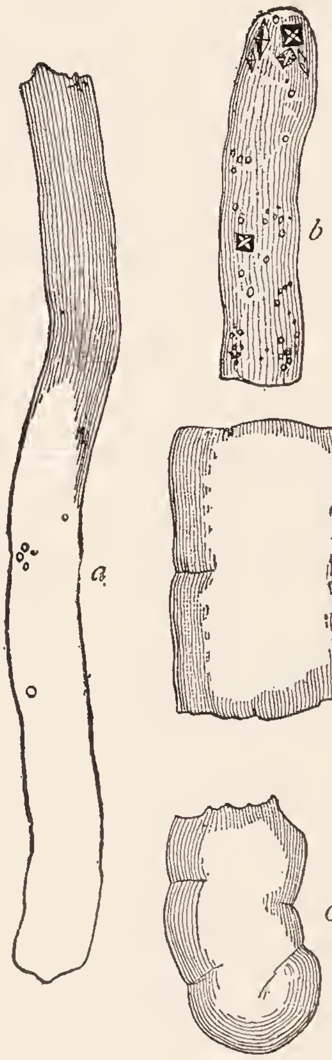


FIG. 111.—*a* and *c*, Waxy casts (Jaksch); *b*, a cast containing crystals of oxalate of lime. *Greatly magnified.*

of women large translucent flat cells from the vagina are nearly always present.

Tube-casts.—As a result of structural mischief in the kidney, there are formed in the tubules cylindric casts of coagulable

material, which is sometimes fibrin, sometimes mucoid matter, and sometimes the plastic substance resulting from the disintegration of the cellular lining. Individually they are too small to be seen by the naked eye, but in the amount usually collected they appear as a light-gray sediment, or perhaps as a cloud at or near the bottom of the glass vessel. Under the microscope they are seen to be minute cylinders, sometimes glassy, sometimes opaque and granular, and sometimes displaying cells. They can be classified accordingly as epithelial, hyaline, granular, fatty, and those made of blood-disks. If in doubt as to the nature of the material composing the casts, staining may be resorted to. The best results are obtained by fixing the sediment to the slide with gentle heat and staining the casts with solution of Sudan III. (which detects

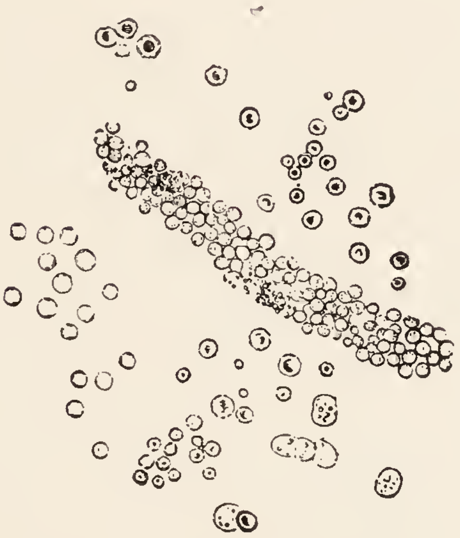


FIG. 112.—Red blood-corpuscles, partly as *rings*, and casts of red blood-corpuscles (Eichhorst). *Greatly magnified.*

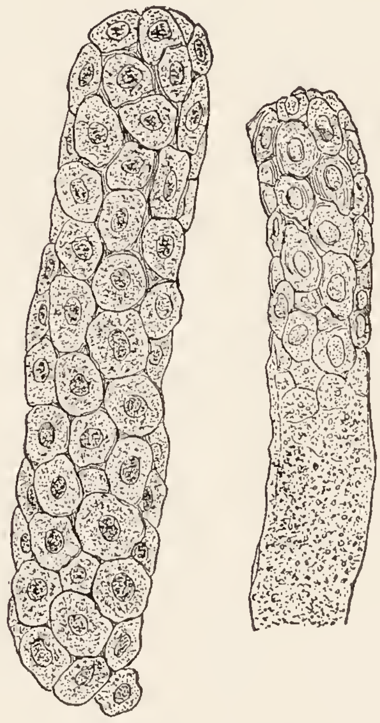


FIG. 113.—Epithelial casts (Jaksch). *Greatly magnified.*

fatty change) and iodin, which distinguishes the amyloid or waxy cast.

Epithelial casts have opaque spheric renal cells imbedded in some plastic matrix. By the number of these one can judge of the activity of the desquamative process in cases of nephritis. They are usually found in acute nephritis (see Fig. 113).

Hyaline casts are always transparent, and sometimes require skilful arrangement of light to show them at all. In case of doubt they may be stained with methylene-blue. They can be grouped in two subvarieties, in one of which, the mucous, would be placed those that are soft and of delicate outline; in the other, the waxy, those that are well defined and brittle.

The mucous casts alone are sometimes found without any other sign of nephritis, and hence must be regarded as not always

of serious import. The waxy casts, on the contrary, are never found but when the kidneys are diseased (see Figs. 110 and 111).

Granular casts (Fig. 114), as the name indicates, are composed of or contain opaque granules which have a yellowish hue. The material may be mucoid or waxy, or such material as is produced by cellular débris.

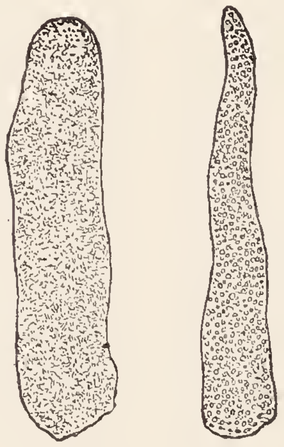


FIG. 114.—Granular casts (Jaksch). *Greatly magnified.*

Fatty casts are such as have fat particles in the matrix, with or without the other bodies mentioned above. If numerous, they are regarded as evidence of fatty change in the kidney.

Blood casts (Fig. 112) are reddish and opaque; they are literally minute clots of blood which have taken shape from the tubules into which the effusion occurs. The corpuscles may be so packed as to be pressed out of their biconcave shape and appear as reddish circles.

Practical Import.—It has been stated under previous sections that if albuminuria or hematuria or an epithelial deposit be of renal origin, careful search of several portions of the deposit with the microscope will most likely find tube-casts. It occasionally happens in cases of Bright's disease that the albuminuria will disappear, and still the casts can be found in the urine. Hence much importance is attached to them in renal diagnosis. As regards the significance of particular varieties, it must be noted that if the mucous cast alone be present, it does not prove nephritis, but any of the other varieties would do so.

It often happens that several varieties occur in the same sample: this probably denotes that the lesion is at different stages in different parts of the organ.

Cystin.—This substance contains sulphur, the composition being expressed by the formula $C_6H_{12}N_2S_2O_4$. One product of its decomposition is the gas hydrogen sulphid; hence a test for it is to boil the suspected material with a solution of lead oxid in sodium hydroxid. If cystin be present, it will form a black precipitate of lead sulphid. As it is very sparingly soluble in water, any considerable amount in the urine would not remain in solution, but be deposited. The deposit is usually abundant, light, and to the naked eye resembles amorphous urates. Unlike urates, it is not dissolved by heat, though it is soluble in ammonia and also in the vegetable acids. When a drop of the ammonia solution is exposed uncovered on a glass slide, it deposits crystals which the microscope shows to have the form of hexagonal tablets (Fig. 84).

The extensive use of iodoform for surgical dressings has been

the source of a fallacy. The crystals of iodoform, accidentally mixed with the urine and viewed by the microscope, will present hexagonal tablets not unlike those of cystin. The chemical reaction is wholly different, and the pronounced odor of iodoform should at once excite suspicion.

Practical Import.—Cystin exists in the protein molecule as a preformed group which is liberated in the tissues and destined to be further decomposed. Certain rare individuals and families, from causes not ascertained, have the anomaly of metabolism which results in a failure to break down the cystin and leads to its appearance in the urine. When present there, it is usually in considerable quantities. Patients do not apparently suffer in health, but the deposited cystin eventually forms a concretion in the bladder.

Leucin and Tyrosin.—These two substances are considered together, because they are by-products of the same processes of

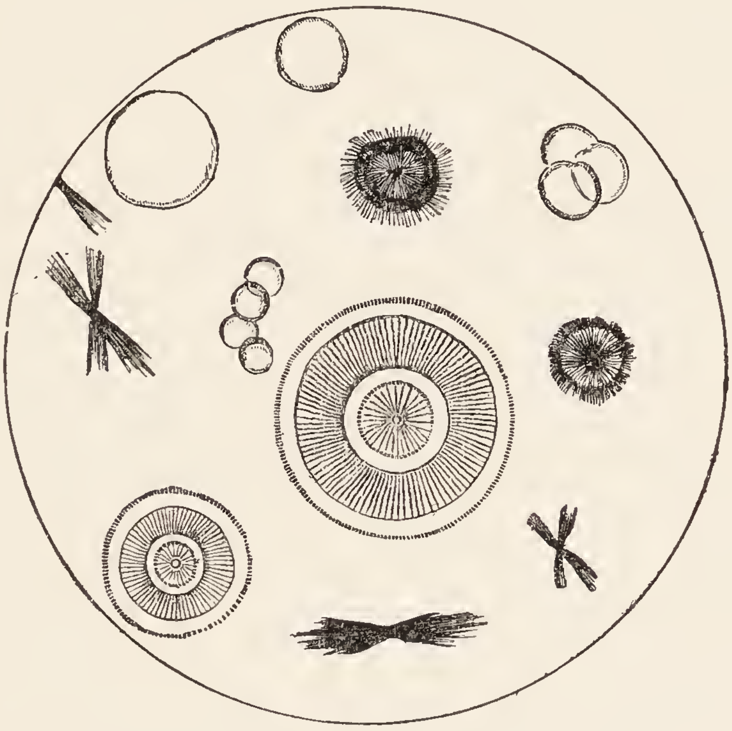


Fig. 115.—Leucin and tyrosin (Laache).

digestion, and when from disease certain biliary matters appear in the urine, these can be found also. Tyrosin is recognized by its turning red when boiled with Millon's reagent of mercuric nitrate; when another portion is carefully warmed with sulphuric acid and then treated with a drop of ferric chlorid, it yields a violet color. In the urine tyrosin may be in solution or it may be thrown down spontaneously as a greenish-yellow deposit. The microscope will resolve this deposit into bundles of yellow acicular needles in radiating stars, crosses, or sheaves (p. 532).

Leucin, being more soluble, is less apt to form a spontaneous deposit, but if a few drops of the suspected urine are allowed to

evaporate by exposure on a glass slide, both leucin and tyrosin will appear in the residuum. Under the microscope leucin is recognized as greenish-yellow globes with concentric markings or radiating spines. If the deposit be touched with a drop of nitric acid, cautiously evaporated to dryness, and then moistened with sodium hydroxid, the leucin residue will turn yellow or brown (p. 505).

Practical Import.—These two bodies are found with icterus in certain maladies when the liver is seriously involved, as in acute yellow atrophy of the liver, phosphorus-poisoning, typhoid, and yellow fever.

Spermatozoa.—These bodies, if present in considerable number in the urine, form a whitish cloud. When taken up with the pipet, the sperm detaches as a thready, drop-like, viscid mucus. When only a few are present, they impart no marked naked-eye property, and in looking for them with the microscope, unless a proper oblique light be used, they may escape observation. In the urine they lose at once their vibratile motion, and yet for days retain their structural characters, the small, transparent oval body or head with the very attenuated cilium, the whole being only $\frac{1}{600}$ in. long.

Practical Import.—Before drawing conclusions as to their significance, it must be ascertained if the sample containing them be not the first micturition after coitus. If not, they may be the washing out of the remains of a nocturnal emission of semen. Their only important relation is as an indication of spermatorrhea—*i. e.*, the escape of sperm independent of the sexual act occurring during the waking hours.

Pneumaturia.—It is a very rare symptom for the last portion of urine to be accompanied by the passage of air from the urethra. This is sometimes associated with tympany of the bladder and may be the result of accidental introduction of air during irrigation of the bladder or as the result of knee-breast position for examination of the bladder. Another group of cases is due to an organism, like the *Bacterium lactis aërogenes*, which develops an odorless gas, usually hydrogen. A third group includes those in which there is a fistulous opening, admitting gas from the rectum and from abscesses.

Micro-organisms.—As it is a fluid containing more or less organic matter in solution, the urine is a fertile medium for the development of microscopic vegetation. The spores or germs of these minute plants come from the containing vessels or from the dust that floats in the air.

The common molds, such as penicillium, appear in a few days on a stale urine. They are seen microscopically as minute jointed

threads matted together in a mycelium. Saccharine urine furnishes the soil for the growth of the yeast fungus, *Saccharomyces cerevisiæ*, the spores of which may be derived from the floating dust of the air. It may be of value as corroborating other evidence of the presence of sugar. The latter plant is recognized as oval cells with granular contents and nuclei multiplying mainly by buds, but sometimes by spore-bearing stems. Even before discharge the sarcinæ of the bladder will reproduce in the urine, and be the cause of obscure vesical symptoms. Their microscopic structure is peculiar from the cubic form of the little masses made by the reproduction of the more minute round particles. The bacteria of putrefaction, the *Micrococcus ureæ*, vibriones, and other similar organisms will flourish not only in the urine outside, but even before micturition. They are identified as extremely minute rods or granules, single or threaded, still or vibratory.

Staining.—With a pipet a small drop of the sediment is transferred to the slide and spread in a thin film. To fix the cells and organisms the film may be set aside to dry spontaneously or be heated over a flame cautiously for three minutes, keeping the heat of the slide below a point painful to the skin of the hand. When dry, it is bathed in a few drops of solution of carbol fuchsin, which stains bacteria and tissue-cells. Heat is again applied and the film again stained by applying for three minutes Gabbet's blue solution, which makes most pathogenic organisms blue, but leaves the tubercle bacilli red.

When the *gonococcus* is sought, the first stain to be used must be eosin and the second methylene-blue.

Practical Import of the Bacteria.—A highly important significance of bacteria in the urine depends upon the fact of their causing decomposition of the urea while still in the bladder. If the ammoniacal products be detained in the bladder, they are very apt to cause cystitis. It is of the greatest importance to guard against the introduction of their germs by means of unsterilized instruments, such as catheters and sounds. It is possible for them to get access to the urine in the bladder from the purulent discharges of a deep-seated gonorrhea or gleet. In paralysis of the bladder they appear to have the power of spontaneous entrance. In that event the harm they may do must be obviated, as far as possible, by frequent and thorough evacuations of the bladder and washings with antiseptic fluids.

When the specific pathogenic bacteria are looked for, it must be with high-power immersion lenses and substage condensers after drying and staining the residue by the approved methods of bacteriology.

It must be noted that the urine in passing through the urethra

of healthy subjects may wash out micro-organisms that colonize there. Among these is mentioned a diplococcus resembling the gonococcus of gonorrhea in all respects save that it is not found in pus-corpuscles, a large streptococcus, and even a bacillus which neither by form nor by staining can be distinguished from the tubercle bacillus. The doubtful bacillus is usually seen singly, whereas the bacilli coming from ulcerating urogenital tuberculosis are generally in groups or crowds considerable in number, like those of a pure culture (Fig. 116). Inoculation experiments would serve to distinguish them from the non-tubercular bacilli. The coexistence of hectic fever and wasting with pyuria and masses of these bacilli in the sediment would prove highly confirmatory of their tubercular origin.

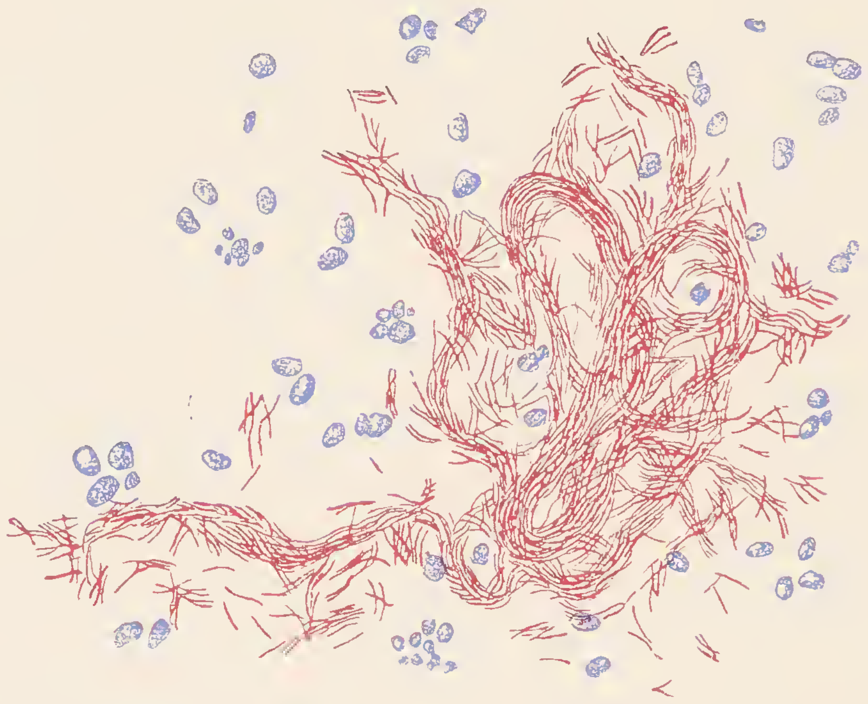


FIG. 116.—Pure culture of tubercle bacilli in the urine in tuberculosis of the genito-urinary apparatus (Zeiss's homogeneous immersion $\frac{1}{12}$; eye-piece No. 4; drawn with a camera lucida; magnified about 1100) (Vierordt).

When the pathogenic bacteria are made out in the sediment unmistakably by form and number, they point to the specific associated disease—the tubercle bacilli to miliary tuberculosis, the erysipelas cocci to erysipelatous nephritis, the pus micrococci to pyemia or endocarditis, the gonococcus to gonorrhea.

The hooklets of echinococcus may be found in the urine, denoting the presence of hydatid cysts somewhere in or about the urinary apparatus. Other parasites occasionally seen in the urine of persons who have lived in the tropics are *Distoma hæmatobium*, *Strongylus gigas*, and *Filaria sanguinis*.

Ehrlich's Typhoid Diazo-reaction.[1]—In 95 per cent. of the

[1] *Artificial diazo-urine* for students' practice may be made by adding to 10 c.c. of urine 1 c.c. of a solution of alpha-naphthylamin (0.1 gm. in 10 c.c. of water and 5 c.c. of hydrochloric acid).

cases of typhoid fever an unknown chromogen appears in the urine, which develops a red color under the conditions of the following test: Two solutions are made up and kept in separate bottles; one contains 1 gm. of sulphanilic acid dissolved in water 95 c.c., with hydrochloric acid, 5 c.c. The other is 0.5 gm. of sodium nitrite in 100 c.c. of water. The test is made by mixing $\frac{1}{2}$ c.c. of the sodium nitrite with 50 c.c. of the sulphanilic-acid solution, and to a suitable amount adding an equal volume of the urine. The two are shaken together and ammonium hydrate is cautiously poured in to overlay the mixture. At the line of contact normal urine will appear more or less orange, while pathologic urine gives a garnet red. The red color will color the foam when the mixture is shaken, and if the test-tube be emptied into a basin of water, a salmon color is produced (Plate 8, Fig. 12).

Practical Import.—This reaction is commonly present in typhoid fever, is rarely absent in septicemia, and has been frequently observed in tuberculosis.

FALLACY.—A similar reaction occurs from the presence of salicylic acid, phenacetin, antipyrin, and other aromatic compounds, as the result of their administration.

They must be excluded from the regimen of the patient before the test can be regarded as significant.

Russo's Methylene-blue Test.—Four drops of a 1 : 1000 aqueous solution of methylene-blue is added to 5 c.c. of suspected urine. A positive reaction changes the blue color to mint- or emerald-green. By repeating the test with normal urine a standard is obtained for detecting fine shades of green. This green color is unaffected by boiling, or by the previous ingestion of quinia, calomel, salol, or phenacetine. Bilirubin will cause the same reaction.

Practical Import.—It is as simple as the diazo-reaction, but of greater diagnostic value. On the second day of typhoid fever a mint-green color is produced, which reaction persists throughout, changing at a later stage to emerald. A favorable outcome may be expected as the tint changes toward the original blue. A positive reaction is observed also in chronic tuberculosis, measles, and small-pox, but no greenish change is seen in miliary tuberculosis, scarlet fever, malaria, and appendicitis. It is especially valuable in differentiating typhoid fever from miliary tuberculosis.

Formaldehyd After Taking Hexamethylenamin.—Before making examinations of the urinary tract and as a routine in managing infections of the upper and middle portions, it is customary to give hexamethylenamin by the mouth, with the expectation that it will be broken up in the kidneys into the antiseptic formaldehyd. For some reason not known this breaking up occurs in less than 50 per cent. of the cases. It is desirable to know if any given patient naturally

makes this transformation. The urine may be tested in one hour after the dose by **Rimini's test**: To 10 c.c. of urine add—(1) solution of phenylhydrazin hydrochlorid (0.5 per cent.), 3 drops; (2) solution sodium nitroprussid (5 per cent.), 3 drops; (3) saturated solution sodium hydroxid, a few drops run down the side of the tube. If formaldehyd be present, a purple color appears, changing to green, and finally to pale yellow. If absent then the color is red changing to light yellow. This test is useful in case of liquid foods, aqueous or alcoholic extracts of solid food, and may be applied directly to milk. When formaldehyd is present more than 1 part in 70,000 to 80,000, a green or bluish-green reaction is obtained. In more dilute solutions the green tint becomes less marked and a yellow tending toward greenish brown is formed.

Urinary Concretions.—In four-fifths of the cases urinary concretions are composed of uric acid and urates. Calcium oxalate, or *mulberry calculi*, stand next in the frequency. The rarer primary varieties are blood concretions, cystin, xanthin, calcium phosphate, calcium carbonate. Secondary to any of these there occurs at the last stage in the history of a calculus a deposit of mixed phosphates. These form a white crust, precipitated upon the calculus as a result of ammoniacal decomposition in the urine changing the reaction and making the phosphates insoluble.

A concretion should be sawed through the middle, so as to expose its concentric layers. A small portion of each distinct layer may be examined by the following procedures:

Calcine a portion of the powder on platinum foil in a Bunsen burner or blowpipe flame:

A. It chars and leaves but little ash = (uric acid, urates, cystin, xanthin, blood).

It gives murexid reaction = (uric acid or urates).

It dissolves in boiling water = (urates).

It does not dissolve in boiling water = (uric acid).

Cystin and xanthin are very rare; the first can be recognized by its test given in another place.

B. It chars very slightly and leaves very much ash = (phosphates, oxalate, or carbonate of calcium).

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